PB84-141514

Sulfide Precipitation of Heavy Metals Effect of Complexing Agents

Kentucky Univ., Lexington

Prepared for

Industrial Environmental Research Lab.
Cincinnati, OH

Jan 84

U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-141514

EPA-600/2-84-023
January 1984

SULFIDE PRECIPITATION OF HEAVY METALS: EFFECT OF COMPLEXING AGENTS

by

D. Bhattacharyya and Y. Ku
Department of Chemical Engineering
University of Kentucky
Lexington, Kentucky 40506-0046

Cooperative Agreement No. CR-807760

Project Officer

Alfred B. Craig, Jr.
Industrial Pollution Control Division
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-600/2-84-023

2.

3. RECIPIENT'S ACCESSION NO.
PB84 141514

4. TITLE AND SUBTITLE
Sulfide Precipitation of Heavy Metals: Effect of Complexing Agents

5. REPORT DATE
January 1984

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
D. Bhattacharyya and Y. Ku.

8. PERFORMING ORGANIZATION REPORT NO.
EPA 6001

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Department of Chemical Engineering
University of Kentucky
Lexington, KY 40506

10. PROGRAM ELEMENT NO.
CBGB1C

11. CONTRACT/GRANT NO.
CR 807760 (Phase I Report)

12. SPONSORING AGENCY NAME AND ADDRESS
U.S. EPA
Industrial Environmental Research Lab.
Industrial Pollution Control Division
Cincinnati, Ohio 45268

13. TYPE OF REPORT AND PERIOD COVERED
Final Phase I Report

14. SPONSORING AGENCY CODE
EPA/600/12

15. SUPPLEMENTARY NOTES
Phase I Report

16. ABSTRACT
Sulfide precipitation behavior of heavy metal ions in the presence of chelating agents was evaluated in terms of type of metal ion, chelating agent type and concentration, pH, sulfide dosage and reaction time. Theoretical solubilities of metal sulfides were calculated for the various metal-sulfide-chelating agent systems and compared with the experimental values. Experiments with Zn and Cd showed that K_{sp}'s of ZnS and CdS of fresh precipitates were one or two log cycles higher than the aged precipitate K_{sp} values. With metal sulfides of higher solubilities (such as, zinc and nickel), high concentrations (greater than 100mg/l) of strong chelating agent (such as EDTA) substantially reduced the extent of sulfide precipitation.

For sparingly soluble metal sulfides (such as, copper and cadmium), the effect of chelating agent was insignificant; residual concentration of less than lmg/l was obtained even with the strong chelating agent at a pH 4. The presence of high concentration of citrate caused partial dissolution of copper sulfide. NiS precipitation was effective only for short reaction times (less than 5 minutes) or in the absence of oxygen. CdS precipitation was effective even in the presence of a strong chelating agent, but the removals of cadmium were interfered in the Ni-containing systems. Continuous experiments were also conducted to evaluate the effectiveness of settling operation and to establish selective metal sulfide separation.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Sulfide Precipitation Metal Finishing Electroplating Chelating Agents		

18. DISTRIBUTION STATEMENT
Release Unlimited

19. SECURITY CLASS *(This Report)*
Unclassified

20. SECURITY CLASS *(This page)*
Unclassified

21. NO. OF PAGES
130

22. PRICE

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

When energy and material resources are extracted, processed, coverted, and used, the related pollutional impacts on our environment and even or our health often require that new and increasingly more efficient polution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report describes work undertaken to evauate the effectiveness of sulfide precipitation of heavy metals in the presence of complexing agents. The technical data obtained in this work can be used for the design of metal precipitation processes over a broad pH range.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

Sulfide precipitation behavior of heavy metal ions in the presence of chelating agents was evaluated in terms of type of metal ion, chelating agent type and concentration, pH, sulfide dosage and reaction time. Theoretical solubilities of metal sulfides were calculated for the various metal-sulfide-chelating agent systems and compared with the experimental values. Experiments with Zn and Cd showed that K_{sp}'s of ZnS and CdS of fresh precipitates were one or two log cycles higher than the aged precipitate K_{sp} values. With metal sulfides of higher solubilities (such as, zinc and nickel), high concentrations (greater than 100mg/l) of strong chelating agent (such as EDTA) substantially reduced the extent of sulfide precipitation.

For sparingly soluble metal sulfides (such as, copper and cadmium), the effect of chelating agent was insignificant; residual concentration of less than 1mg/l was obtained even with the strong chelating agent at a pH 4. The presence of high concentration of citrate caused partial dissolution of copper sulfide. NiS precipitation was effective only for short reaction times (less than 5 minutes) or in the absence of oxygen. CdS precipitation was effective even in the presence of a strong chelating agent, but the removals of cadmium were interfered in the Ni-containing systems. Continuous experiments were also conducted to evaluate the effectiveness of settling operation and to establish selective metal sulfide separation.

This report was submitted in fulfillment (Phase I) of Cooperative Agreement No. CR-807760 by the University of Kentucky under the sponsorship of the U.S. Environmental Protection Agency.

CONTENTS

Foreword iii
Abstract iv
Figures. vi
Tables xi

1. Introduction 1
2. Complexation Reaction Models 4
    Dissociation of Complexing Agent. 5
    Metal Complexation Equilibrium. 8
3. Precipitation Reaction Models. 17
    H_2S-HS^--S^{2-} Equilibrium 17
    Metal-Sulfide Reaction. 19
    Metal-Sulfide-Chelating Agent Reaction. 26
4. Experimental 44
    Equipment 44
    Procedure 52
5. Results and Discussions. 56
    Na_2S-Water System 57
    Sulfide Precipitation of Solutions Containing Single Heavy Metal Ion in the Presence of Chelating Agents. 58
        Zinc sulfide precipitation 58
        Copper sulfide precipitation 71
        Cadmium sulfide precipitation. 83
        Nickel sulfide precipitaiton 85
    Sulfide Precipitation of Solutions Containing Multi-Metal Ions. 91
    Continuous Systems for Sulfide Precipitation. 99
        Single metal systems 99
        Multi-metal systems. 99
6. Summary and Conclusions. 105

References. 118

FIGURES

Number		Page
1	Distribution of Various Species of EDTA in Aqueous Solution as a Function of pH	7
2	Conditional Stability Constants of Various M-EDTA Complexes as a Function of pH	13
3	Distribution of Various Species in Cu^{2+}-EDTA System as a Function of pH	15
4	Distribution of Various Species in Cd^{2+}-EDTA System as a Function of pH	16
5	H_2S-HS^--S^{2-} Equilibrium	18
6	Calculated Solubilities of Zinc, Copper, and Nickel Sulfides as a Function of pH at Fixed Equilibrium Soluble Sulfide (S_T) Concentration.	22
7	Comparison of the Solubilities Between Metal Sulfides and Metal Hydroxides at Various pH Values.	24
8	Reaction for Metal-Sulfide-Chelating Agent System	27
9	Calculated Solubility of ZnS as a Function of pH in the Presence of Various Chelating Agents	32
10	Calculated Solubility of ZnS as a Function of Soluble Sulfide Concentration in the Presence of EDTA	34
11	Effect of Sulfide Dosage and pH on Calculated ZnS Solubility in the Presence of EDTA	35
12	Calculated Solubility of ZnS as a Function of EDTA Concentration for Various pH Values	37
13	Calculated Solubility of CuS as a Function of pH in the Presence of Various Chelating Agents	38
14	Calculated Solubility of CdS as a Function of pH in the Presence of Various Chelating Agents	39

Number Page

15 Calculated Solubility of NiS as a Function of pH in the Presence of Various Chelating Agents 40

16 Comparison of Metal Sulfides and Metal Hydroxide Solubilities as a Function of pH in the Presence of EDTA 41

17 Solubility of $Zn(OH)_2$ as a Function of pH in the Presence of Various Chelating Agents 43

18 Schematic Diagram of Batch Unit 47

19 Schematic Diagram of Continuous Unit. 49

20 Effect of EDTA Concentration on ZnS Precipitation. 61

21 Effect of pH on ZnS Precipitation in the Presence of Various Concentrations of EDTA 65

22 Effect of pH on ZnS Precipitation in the Presence of Citrate. 67

23 Effect of Sulfide Dosage on ZnS Precipitation in the Presence of EDTA. 68

24 Effect of Reaction Time on ZnS Precipitation in the Presence of Various Chelating Agents. 70

25 Effect of EDTA Concentration on CuS Precipitation. 73

26 Effect of Na_2S Dosage on CuS Precipitation in the Presence of EDTA. 75

27 Effect of pH on CuS Precipitation in the Presence of EDTA 76

28 Effect of Reaction Time on CuS Precipitation in the Presence of Chelating Agents. 79

29 Effect of Reaction Time on CuS Precipitation in the Presence of Various Concentration of Citrate 80

30 Comparison of CuS Precipitation in Open System and N_2 Atmosphere for Cu-Citrate System. 81

Number Page

31 Effect of EDTA Concentration on CdS Precipitation. 87

32 Effect of pH on CdS Precipitation in the Presence of EDTA 87

33 Effect of pH on NiS Precipitation in the Presence of EDTA 88

34 Effect of EDTA Concentration on NiS Precipitation. 88

35 Effect of Reaction Time on NiS Precipitation in the Presence of Chelating Agents. 90

36 Effect of Sulfide Dosage on NiS Precipitation for Cd-Ni Mixture as a Function of Reaction Time 95

37 Effect of Sulfide Dosage on CdS Precipitation for Cd-Ni Mixture as a Function of Reaction Time 95

38 Residual Ni Concentration for Cd-Ni Mixture after Sulfide Treatment as a Function of Ni/Cd Ratio. 96

39 Residual Cd Concentration for Cd-Ni Mixture after Sulfide Treatment as a Function of Ni/Cd Ratio. 96

40 Effect of Reaction Time on Residual Metal Concentrations for Cu-Cd-Ni-Zn Mixture 98

41 Effect of Reaction Time on Residual Metal Concentrations for Cu-Cd-Ni-Zn-EDTA Mixture. 98

42 Comparison of Batch and Continuous Experiments under Same Experimental Condition. 100

43 Comparison of Batch and Continuous Experiments for Cu-Cd-Ni-Zn Mixture under Same Experimental Condition 101

44 Effect of EDTA Concentration on Metal Sulfide Precipitate Settling Characteristics for Cu-Cd-Ni-Zn Mixture. 103

Number Page

45 Calculated Solubilities of $Cu(OH)_2$ and CuS as a Function of pH in the Presence of Chelating Agent. 106

46 Effect of Chelating Agent and pH on Metal Sulfide Precipitation (experimental) 107

47 Comparison of Calculated and Experimental Results for ZnS Precipitation (K_{sp}=1.6x10^{-24}). 110

48 Comparison of Calculated and Experimental Results for ZnS Precipitation (K_{sp}=1.6x10^{-22}). 111

49 Comparison of Calculated and Experimental Results for CdS Precipitation (K_{sp}=2.0x10^{-26}). 112

50 Comparison of Calculated and Experimental Results for NiS Precipitation Using Literature K_{sp} 113

51 Relationship between Residual Metal Concentrations and Conditional Solubility Constant x K_{sp} 114

52 Effect of Zn, Ni, and Cu on CdS Precipitation 115

TABLES

Number Page

1 Acid Dissociation Constants of Chelating Agents 6

2 Overall Stability Constants for Various Metal-Chelating Agent Systems. 10

3 Metal-Sulfide Precipitation Reactions 20

4 Comparison of Solubility Product Constants. 25

5 Operational Conditions. 45

6 Sensitivity of Metals Obtained with Varian Atomic Absorption Spectrophotometer. 50

7 Effect of Chelating Agents on ZnS Precipitation 59

8 Effect of Citrate Concentration on ZnS Precipitation. . 63

9 Effect of Chelating Agents on CuS Precipitation 72

10 Effect of pH on CuS Precipitation in the Presence of Citrate 77

11 Comparison of Residual Metal Concentrations Obtained with Three Different Microfilters for Metal-Na_2S-EDTA System 82

12 Comparison of Sulfide Precipitation for Various Metals Containing EDTA 84

13 Effect of Chelating Agents on CuS Precipitation 86

14 Sulfide Precipitation of Cu-Zn Mixture in the Presence of EDTA 92

SECTION 1

INTRODUCTION

Process wastewaters containing heavy metals result from metal finishing and production operations and certain inorganic chemical manufacturing operations. Depending on their origin, these process wastewaters may also contain chelating agents such as EDTA, citrate, etc. The effective removal of heavy metals or their selective recovery, even at high pH, is often not feasible by conventional hydroxide precipitation. Sulfide precipitation is an alternate method for the effective treatment of industrial wastewaters containing highly toxic heavy metals and this method is especially effective when complexing or chelating agents are present in the wastewaters.

Hydroxide precipitation of heavy metals (1-4) is the most often used method for treating industrial wastewaters. Metals are removed by adjusting the pH of the wastewater with lime or caustic soda, to the point where the metals exhibit minimum solubilities. The metal hydroxides can be removed by flocculation and sedimentation. Some common limitations of the hydroxide process are:

- Hydroxide precipitates tend to resolubilize if the solution pH is increased or decreased from their minimum solubility values; maximum removal efficiency may not be achieved unless the pH is controlled over a narrow range.

- The theoretical minimum solubility for different metal hydroxides occurs at different pH values. Hence, the removal of metals by hydroxide precipitation of mixed metal wastes may not be effective.

Sulfide precipitation has been demonstrated to be an effective alternative to hydroxide precipitation (5-15) for removing various heavy metal ions from industrial wastewaters. An extensive bench-scale study was conducted by Bhattacharyya et al. (5) for the purpose of evaluating the effectiveness of sulfide precipitation using Na_2S. Their investigation have shown that high metal removal efficiencies can be achieved. Several of the literature citations mention the effect of chelating agents on sulfide precipitation, however, no quantitative research of this effect has been reported in the literature under various operating conditions for metal sulfide precipitations. Since metal chelates are highly dissociated at low pH values, effective metal removal by sulfide precipitation is possible even at pH 3-4. It is also possible to obtain selective precipitation of heavy metal sulfides by the addition of proper chelating agents.

The overall objective of this investigation was to establish the extent of precipitation of selected heavy metals with sodium sulfide in the presence of several commonly used chelating agents. Extensive bench-scale experiments were conducted with several synthetic systems.

The specific objectives were:

1. To determine the residual metal concentrations that could be achieved for the heavy metal ions Zn, Cu, Cd, and Ni in the presence of various chelating agents.

2. To establish the effects of pH, Na_2S dosage, metal concentration, chelating agent concentration and reaction time on metal sulfide precipitation.

3. To determine the residual metal concentrations and precipitation behavior of selected multi-metal systems.

4. To determine the residual metal concentrations that could be obtained for several continuous systems with and without chelating agents.

5. To calculate theoretical metal sulfide solubilities in the presence of chelating agents utilizing literature equilibrium values on precipitation reactions, chelation reactions, hydrolysis reactions, and the equilibrium involving $H_2S \rightleftarrows HS^- + H^+ \rightleftarrows S^{2-} + 2H^+$.

SECTION 2

COMPLEXATION REACTION MODELS

Metal complexes are compounds that contain a central metal ion bonded to a cluster of organic or inorganic anions or neutral molecules. The charge of the complex formed may differ from that of the original metal ion. The sign and magnitude of the charge of the complex formed are given by the algebraic sum of the ionic species constituting the complex.

Compounds such as ethylenediaminetetracetic acid (EDTA), 1,2-diaminocyclohexanetetraacetic acid (DCTA), citric acid, oxalic acid and cyanide are commonly used as complexing agents. Compounds such as cyanide, carbonate, that have only one pair of electrons to bond with the central ion are called complexing agents. Compounds such as EDTA, DCTA and citrate oxalates, that are bonded to central metal ion by more than one pair of electrons are called chelating agents. Complex formation with chelating agents is called chelation, and the complexes formed are called chelates. The most obvious feature of a chelate is the formation of a ring. These cyclic chelates have exceptionally high stability and play an important role in aquatic chemistry.

DISSOCIATION OF COMPLEXING AGENTS

In the absence of metal ions, complexing agents may form complexes with a proton, H^+. The stepwise acid dissociation constants for polyprotinated ligands can be expressed as follows.

$$H_nL \rightleftarrows H + H_{n-1}L \qquad (1)$$

$$H_{n-1}L \rightleftarrows H + H_{n-2}L \qquad (2)$$

$$\begin{matrix} \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \end{matrix}$$

$$HL \rightleftarrows H + L \qquad (3)$$

in which "L" stands for ligand.

The corresponding stepwise dissociation constants for several complexing agents are shown Table 1. Using these stepwise dissociation constants, a set of simultaneous equations can be solved to obtain the distribution of various species in the solution under different experimental conditions. A typical species distribution of EDTA are computed and shown in Figure 1 as a function of pH.

TABLE 1. ACID DISSOCIATION CONSTANTS OF CHELATING AGENTS (16)

Complexing Agent	Dissociation Constant (at 25C)			
	pK_1	pK_2	pK_3	pK_4
Citric Acid	3.00	4.40	6.10	16.00
Cyanide	9.20	---	---	---
DCTA	2.51	3.60	6.20	11.78
EDTA	2.07	2.75	6.24	10.34
Gluconic Acid	2.30	4.28	9.67	---
HEDTA	2.40	5.40	10.00	---
NTA	1.89	2.49	9.73	---
Oxalate	1.40	3.80	---	---
Tartrate	2.90	4.10	---	---

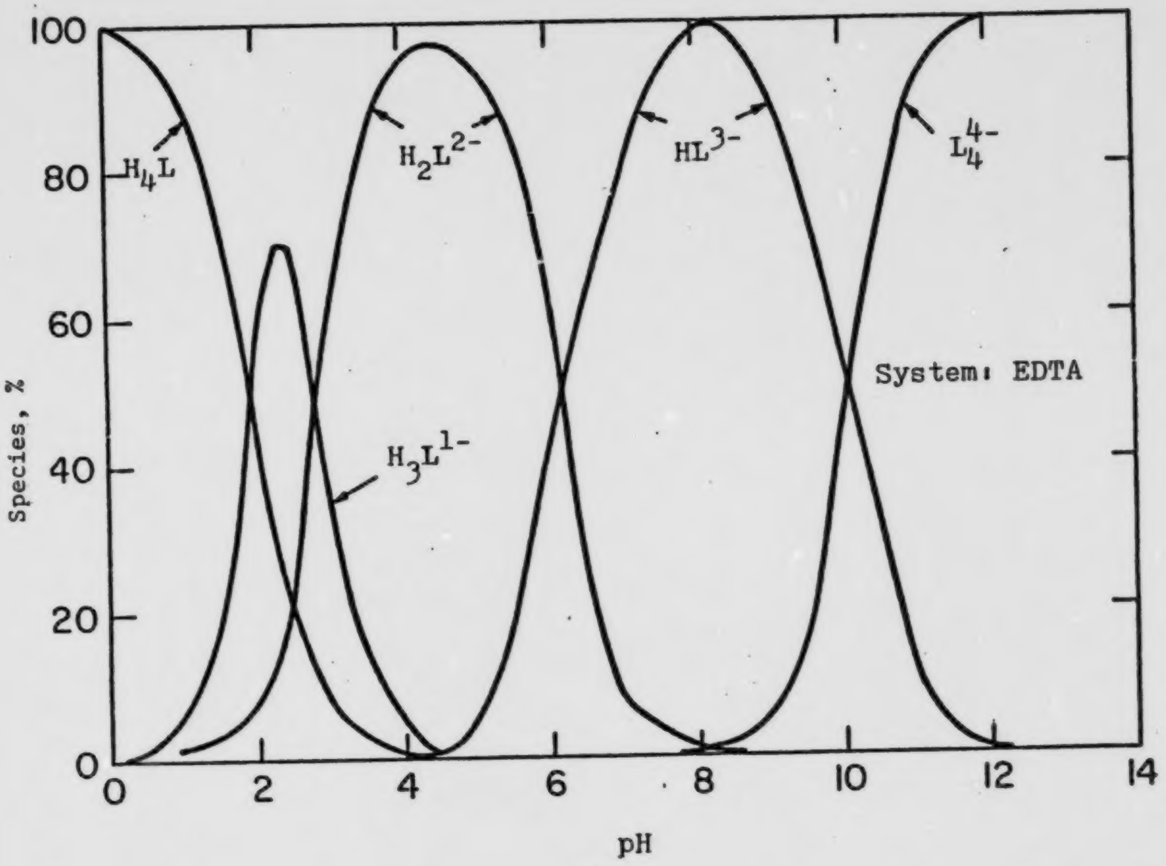

Figure 1. Distribution in Various Species of EDTA in Aqueous Solution as a Function of pH.

METAL COMPLEXATION EQUILIBRIUM

In the presence of metal ions, additional equilibrium have to be taken into account for metal-chelate formation. Besides the equilibria shown between the ligand and proton, ligands also show a series of stepwise equilibria with metal ions, according to the following expressions:

$$M + L \rightleftharpoons ML \tag{4}$$

$$ML + L \rightleftharpoons ML_2 \tag{5}$$

$$\begin{array}{ccc} \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \end{array}$$

$$ML_{n-1} + L \rightleftharpoons ML_n \tag{6}$$

Chelating agents may form complexes that contain protons in addition to the metal ion. These are called protonated complexes (MHL_n, MH_2L_n...). Hydroxy metal complexes ($MOHL_n$, $M(OH)_2L_2$...) may also form. In the case of EDTA (=L), for example, in addition to ZnL, the formation of complexes ZnHL and Zn(OH)L have to be considered for zinc-EDTA chelation. The formation of these complexes can be represented by the general reactions:

$$ML_n + mH \leftrightarrows MH_mL_n \qquad (7)$$

$$ML_n + pOH \leftrightarrows M(OH)_pL_n \qquad (8)$$

At high pH values, the hydroxide ion may compete with complexing agents for the coordinative positions on the metal ion. Metal hydrolysis reactions can be expressed as following:

$$M + OH \leftrightarrows MOH \qquad (9)$$

$$MOH + OH \leftrightarrows M(OH)_2 \qquad (10)$$

$$\begin{array}{ccc} \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \end{array}$$

$$M(OH)_{r-1} + OH \leftrightarrows M(OH)_r \qquad (11)$$

The overall equilibrium of complexes formed in the presence of metal ion can be represented by Equation (1)-(11). The corresponding stability constants of these reactions are shown in Table 2 for several metal-chelating agent and metal hydrolysis reactions. It should be noted that only few complex species may predominate in the various metal-chelating agent systems.

In order to include all the complexation reactions, a concept of apparent stability constant, known as conditional

TABLE 2. OVERALL STABILITY CONSTANTS FOR VARIOUS METAL-CHELATING AGENT SYSTEMS (16)

Ligand	Metal Ion H^+	Cu^{2+}	Cd^{2+}	Ni^{2+}	Zn^{2+}
OH^-	$\mathrm{HL:1.0x10^{14}}$	$\mathrm{CuL:1.0x10^{6}}$	$\mathrm{CdL:2.0x10^{4}}$	$\mathrm{NiL:3.98x10^{4}}$	$\mathrm{ZnL:7.94x10^{4}}$
Citrate	$\mathrm{HL:1.0x10^{16}}$ $\mathrm{H_2L:1.26x10^{22}}$ $\mathrm{H_3L:3.16x10^{26}}$ $\mathrm{H_4L:3.16x10^{29}}$	$\mathrm{CuL:1.0x10^{18}}$ $\mathrm{CuHL:2.0x10^{22}}$ $\mathrm{CuH_2L:2.0x10^{28}}$	$\mathrm{CdHL:1.0x10^{20}}$ $\mathrm{CdH_2L:2.5x10^{24}}$	$\mathrm{NiL:2.0x10^{14}}$ $\mathrm{NiHL:1.26x10^{21}}$ $\mathrm{NiH_2L:2.0x10^{25}}$	$\mathrm{ZnL:2.5x10^{11}}$ $\mathrm{ZnHL:6.3x10^{20}}$ $\mathrm{ZnH_2L:1.0x10^{25}}$
EDTA	$\mathrm{HL:2.19x10^{10}}$ $\mathrm{H_2L:3.8x10^{16}}$ $\mathrm{H_3L:2.14x10^{19}}$ $\mathrm{H_4L:2.51x10^{21}}$	$\mathrm{CuL:6.31x10^{18}}$ $\mathrm{CuHL:6.31x10^{21}}$ $\mathrm{CuOHL:1.58x10^{21}}$	$\mathrm{CdL:2.88x10^{16}}$ $\mathrm{CdHL:2.51x10^{17}}$	$\mathrm{NiL:3.99x10^{18}}$ $\mathrm{NiHL:6.31x10^{21}}$	$\mathrm{ZnL:3.16x10^{16}}$ $\mathrm{ZnHL:7.9x10^{20}}$ $\mathrm{ZnOHL:3.16x10^{19}}$
Gluconic Acid	$\mathrm{HL:6.9x10^{9}}$ $\mathrm{H_2L:8.9x10^{13}}$ $\mathrm{H_3L:1.78x10^{16}}$	$\mathrm{CuL:7.07x10^{7}}$ $\mathrm{CuL_2:2.51x10^{14}}$	$\mathrm{CdL:7.94x10^{3}}$	$\mathrm{NiL:7.94x10^{5}}$ $\mathrm{NiL_2:2.19x10^{10}}$	$\mathrm{ZnL:2.82x10^{5}}$ $\mathrm{ZnHL:2.88x10^{9}}$
Tartrate	$\mathrm{HL:1.26x10^{4}}$ $\mathrm{H_2L:1.0x10^{7}}$	$\mathrm{CuL:1.58x10^{3}}$ $\mathrm{CuL_2:1.26x10^{5}}$ $\mathrm{CuL_3:6.31x10^{5}}$	$\mathrm{CdL:6.31x10^{2}}$	———	$\mathrm{ZnL:4.79x10^{2}}$ $\mathrm{ZnHL:3.16x10^{5}}$
HEDTA	$\mathrm{HL:1.0x10^{10}}$ $\mathrm{H_2L:2.51x10^{15}}$ $\mathrm{H_3L:6.31x10^{17}}$	$\mathrm{CuL:2.51x10^{17}}$	$\mathrm{CdL:1.0x10^{13}}$	$\mathrm{NiL:1.0x10^{17}}$	$\mathrm{ZnL:3.16x10^{14}}$
NTA	$\mathrm{HL:5.39x10^{9}}$ $\mathrm{H_2L:1.7x10^{12}}$ $\mathrm{H_3L:1.3x10^{14}}$	$\mathrm{CuL:1.26x10^{13}}$	$\mathrm{CdL:6.3x10^{9}}$	$\mathrm{NiL:3.2x10^{11}}$	$\mathrm{ZnL:4.57x10^{10}}$

stability constant, has been introduced. (17)

The general expression for the overall conditional stability constant of a complex is

$$K_{ML}' = [ML_n]/[M'] [L']^n \qquad (12)$$

in which $[M']$ denotes conditional molar concentration of the free metal ion in solution plus the concentration of metal bound to other species in solution other than the complex or chelating agent L.

$$[M'] = [M] + [M(OH)] + [M(OH)_2] + \ldots \qquad (13)$$

Similarly, $[L']$ is the conditional free complexing agent ion concentration; $[ML_n']$ is the conditional metal complexing agent concentration.

$$[L'] = [L] + [ML] + 2[ML] + \ldots \qquad (14)$$
$$[ML_n'] = [ML] + [MHL] + [MOHL] + \ldots \qquad (15)$$

Three new quantities $(\alpha_{M'}, \alpha_{L'}, \alpha_{ML'})$ are introduced to facilitate the calculation of species distribution:

$$\alpha_{M'} = [M]/[M'] \tag{16}$$

$$\alpha_{L'} = [L]/[L'] \tag{17}$$

$$\alpha_{ML'_n} = [ML_n]/[ML'_n] \tag{18}$$

If the complexes formed are 1:1 type, the conditional stability constant can be represented as following:

$$K'_{ML} = [ML']/[M'][L'] \tag{19}$$

Combining Equation (4) and (16)-(19), the following expression can be obtained:

$$K'_{ML} = (K_{ML})(\alpha'_{M})(\alpha'_{L})/(\alpha'_{ML}) \tag{20}$$

Figure 2 shows the relationship between K'_{ML} and pH for a number of metal-EDTA systems. The curves go through a maximum. In the low pH range, hydrogen ion competes with the metal ion for complexing agent. As pH value increases, the formation of metal-EDTA complexes is favored by deprotonation of complexing agents, thus increasing conditional stability constant. At higher pH values, the formation of metal hydroxide complexes occurs as a strong competing side reaction, thus reduces the conditional stability constant. For copper, no significant change occurs in

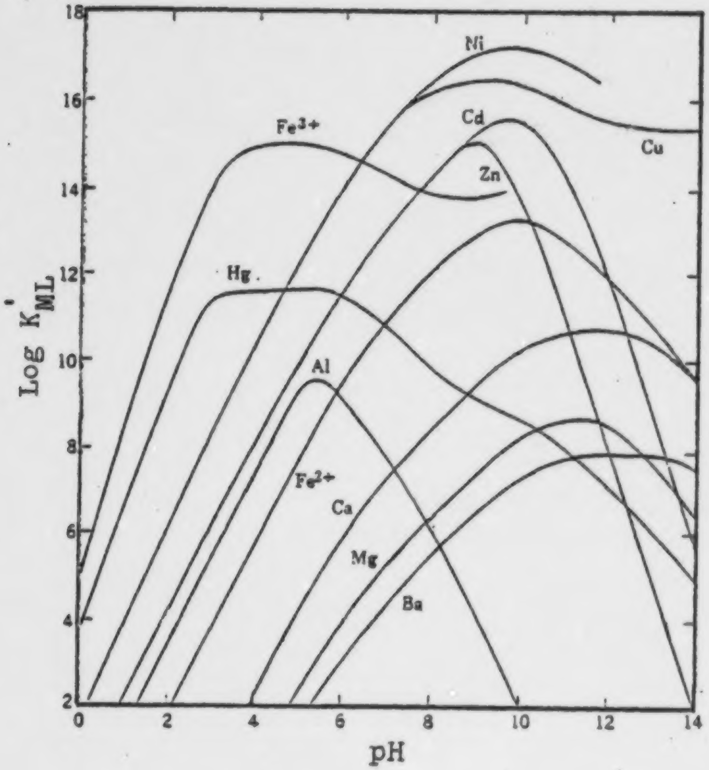

Figure 2. Conditional Stability Constants of Various M-EDTA Complexes as a Function of pH (16).

conditional stability constant at pH value greater than 8.0. This can be explained by the high stability of Cu-EDTA complexes.

The equilibrium concentration of all species present in a metal-complexing agent system can be calculated by solving a series of simultaneous equations (Equation (1)-(11)). A computer program was developed to solve the problem by Cheng (18). The distribution of species for copper- and cadmium-EDTA systems are shown in Figure 3 and 4. These results indicate that the formations of metal chelates are always favorable over metal hydroxides. And over the range of interest (pH 4.0-10.0), the predominate metal complex formed is $M(EDTA)^{2-}$.

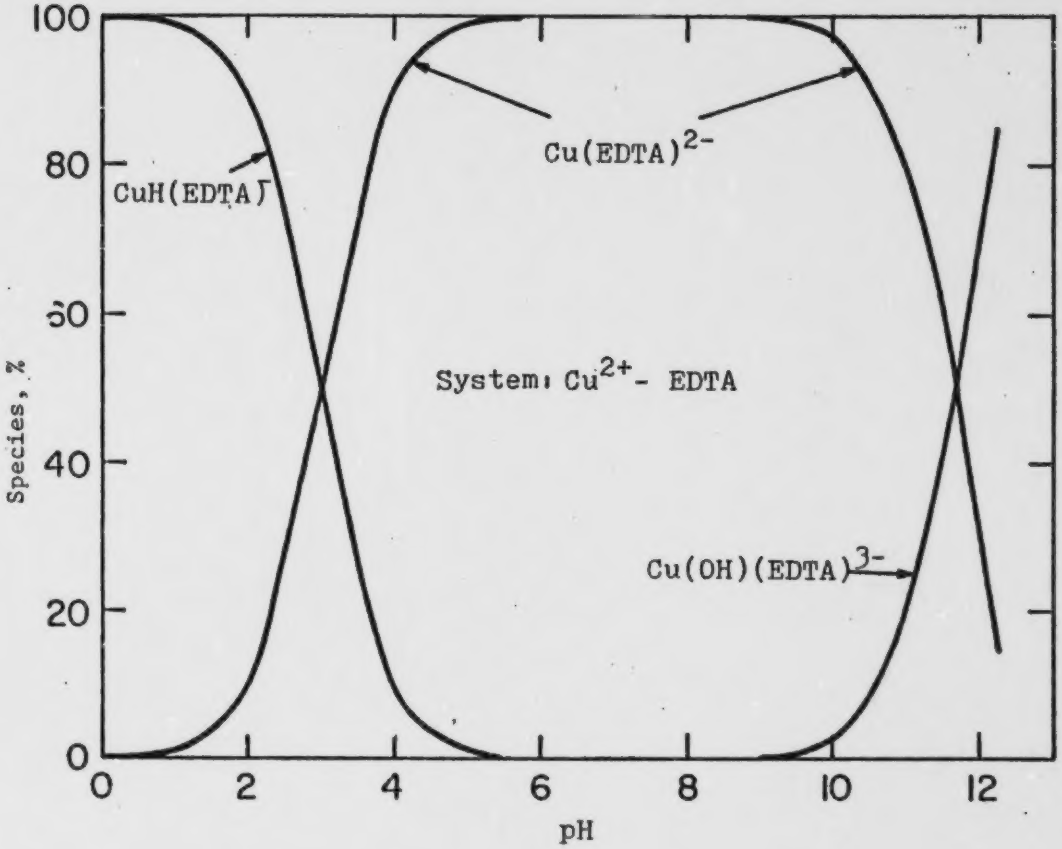

Figure 3. Distributiion of Various Species in Cu^{2+}-EDTA System as a Function of pH.

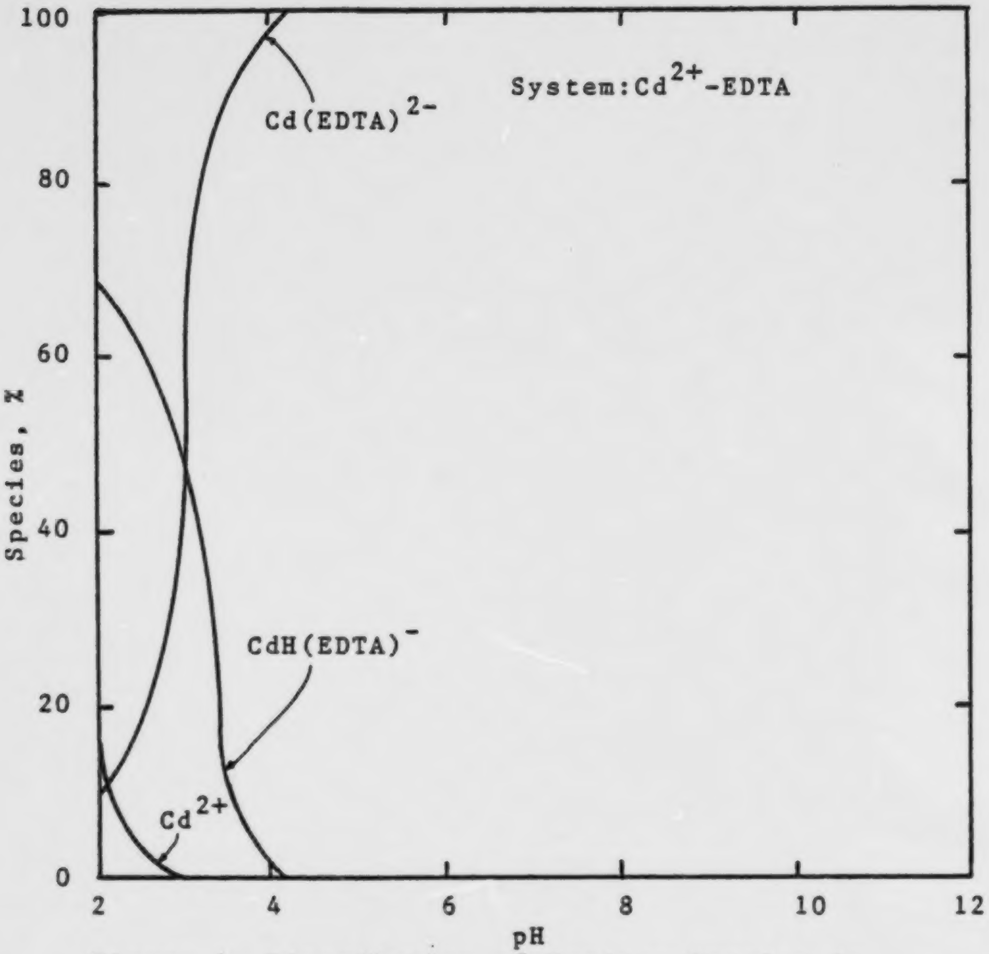

Figure 4. Distribution of Various Species in Cd^{2+}-EDTA System as a Function of pH.

SECTION 3

PRECIPITATION REACTION MODELS

Sulfide precipitation is an effective method to achieve a high degree of separation of various heavy metals from aqueous systems because heavy metals tend to form very insoluble precipitates with sulfide ion. The extent of metal sulfide precipitation is expected to be a function of type of metal, pH, sulfide dosage, temperature and the presence of other interfering ions (such as EDTA, citrate, etc.).

H_2S-HS^--S^{2-} EQUILIBRIUM

When sulfides (Na_2S, NaHS, H_2S) dissolve in water, $H_2S_{(g)}$, $H_2S_{(aq)}$, HS^- and S^{2-} species are present. The solubility of H_2S in water is about 0.1M at 25°C (19). The dissociation of $H_2S_{(aq)}$ follows:

$$H_2S \rightleftarrows H^+ + HS^- \qquad K_1 = 1.0\times10^{-7} \qquad (20)$$

$$HS^- \rightleftarrows H^+ + S^{2-} \qquad K_2 = 1.2\times10^{-13} \qquad (21)$$

A diagram for dominant sulfur species as a function of pH is shown in Figure 5. The figure shows that at pH of less than 5.0,

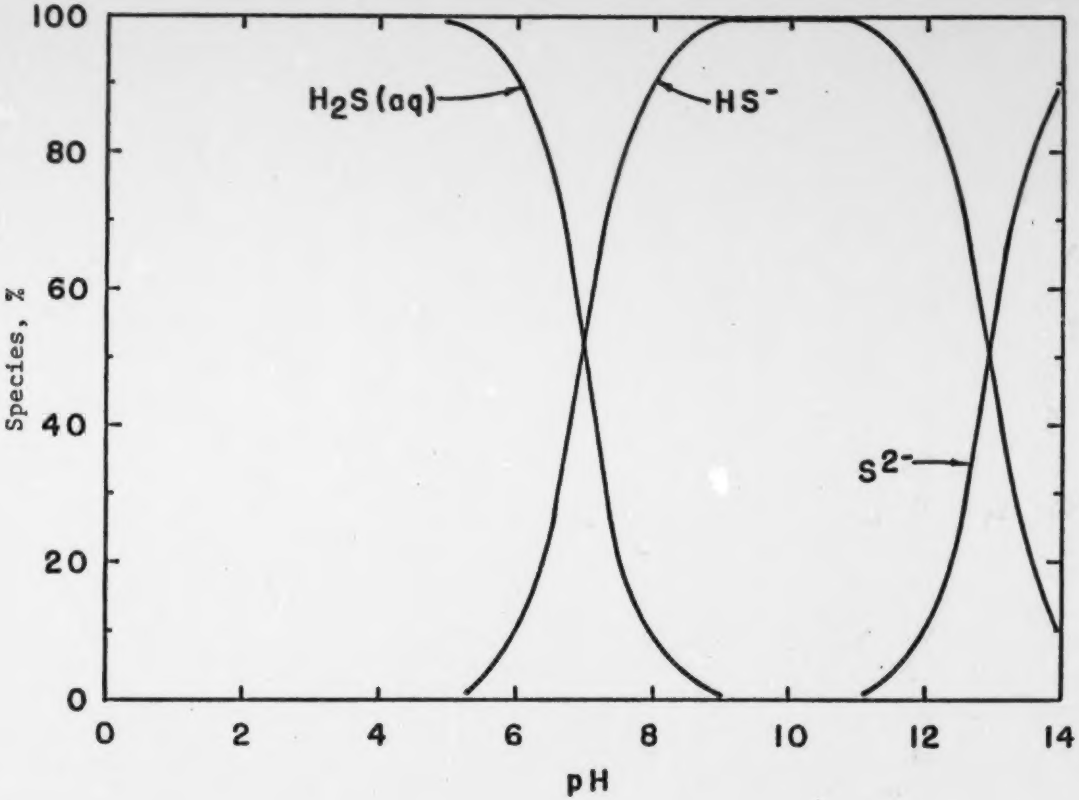

Figure 5. H_2S-HS^--S^{2-} Equilibrium.

the predominate species is $H_2S_{(aq)}$. For pH values greater than 9.0, S^{2-} and HS^- ions are predominate. At low pH values (less than 4.0), part of the H_2S will be lost into air due to $H_2S_{(aq)}$-$H_2S_{(g)}$ equilibrium. For example, at pH 3.0, 68% of $H_2S_{(aq)}$ will be in the gas phase.

METAL-SULFIDE REACTION

Metal sulfide precipitate is formed as the metal cation reacts with sulfide ion in aqueous solution. In the basic media, formation of several metal-hydroxy complexes may also occur. In addition to reactions (20) and (21), the primary reactions that involve divalent heavy metal ions, M^{2+} in metal sulfide precipitation are:

$$M^{2+} + S^{2-} \leftrightarrows MS\ (\text{solid}) \qquad (22)$$

$$M^{2+} + OH^- \leftrightarrows M(OH)^+ \qquad (9)$$

$$M(OH)^+ + OH^- \leftrightarrows M(OH)^- \qquad (10)$$

$$\begin{matrix} \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \end{matrix}$$

$$M(OH)_{r-1}^{r+1} + OH^- \leftrightarrows M(OH)_r \qquad (11)$$

Table 3 shows the equilibrium constants of the above

TABLE 3. METAL-SULFIDE PRECIPITATION REACTIONS

Reaction	Log K (20 , 21)				
	Ni	Zn	Cd	Cu	Pb
$M^{2+} + S^{2-} \rightleftarrows MS(s)$	20.7	23.8	27.7	35.1	27.0
$M^{2+} + OH^- \rightleftarrows M(OH)^+$	4.1	4.4	3.9	7.0	6.3
$M(OH)^+ + OH^- \rightleftarrows M(OH)_2$	5.0	6.9	3.8	3.7	4.6
$M(OH)_2 + OH^- \rightleftarrows M(OH)_3^-$	3.0	2.8	1.0	3.8	3.0
$M(OH)_3^- + OH^- \rightleftarrows M(OH)_4^{2-}$	---	3.5	- 0.05	2.2	---
$H_2S \rightleftarrows H^+ + HS^-$	$K = 1.0 \times 10^{-7}$				
$HS^- \rightleftarrows H^+ + S^{2-}$	$K = 1.2 \times 10^{-13}$				

reactions for several divalent heavy metals. Equation (20)-(22) and (9)-(11) can be solved for any divalent heavy metal by using appropriate solubility constants (Table 3). It should be noted that K_{sp} values of fresh precipitates may be higher than literature values of "aged" precipitates. In addition, some metals (such as Zn, Ni) form more than one type of precipitate (22).

The soluble metal concentration after sulfide precipitation is a function of pH and the equilibrium soluble sulfide concentration, S_T. (S_T is the total sulfide concentration of $H_2S_{(aq)}$, $HS^-_{(aq)}$ and $S^{2-}_{(aq)}$). The diagram of total metal sulfide solubilities (sum of all soluble metal species, including M^{2+} and hydroxide complexes, $M(OH)_n^{n-2}$) of Zn, Cu, Cd, and Ni for different S_T values is shown in Figure 6 at various pH values.

Figure 6 shows that total metal solubilities decrease in acid media as pH increases; but in very basic media, solubilities increases as pH value increases. This is due to the fact that hydrolysis of metal ions becomes important at high pH values. In actual precipitation practice S_T is monitored by a sulfide electrode and S_T should be maintained at less than 1mg/l to avoid toxicity. The extent of precipitation decreases in the order CuS > CdS > ZnS > NiS because solubility products, K_{sp}, control the residual concentration of metal ions. It should be noted that NiS oxidizes (22) in the

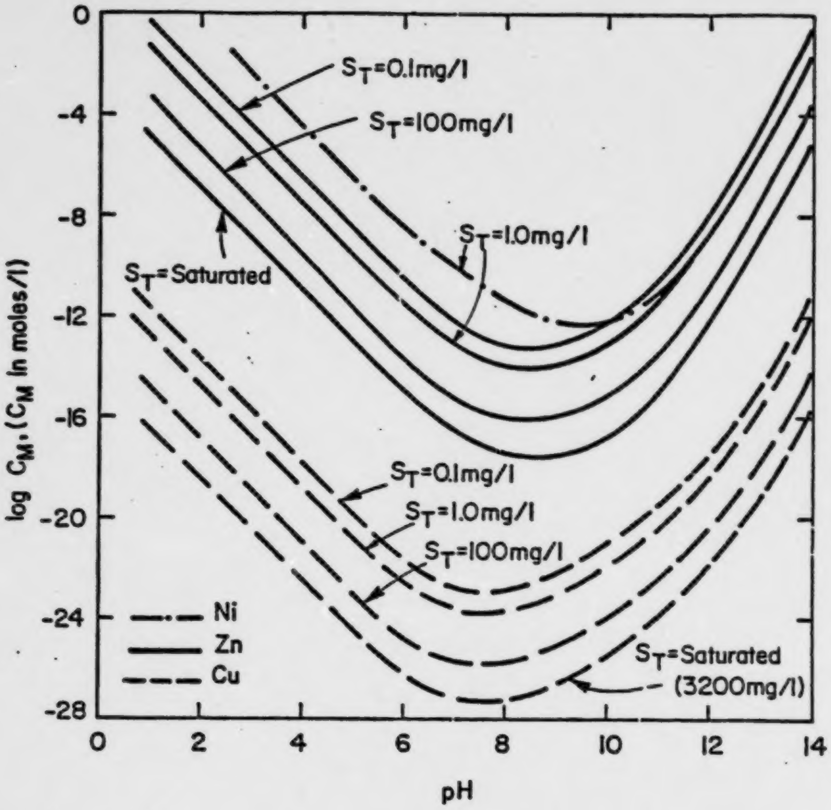

Figure 6. Calculated Solubilities of Zinc, Copper, and Nickel Sulfides as a Function of pH at Fixed Equilibrium Soluble Sulfide (S_T) Concentration (15).

presence of oxygen (at pH 9) and hence the NiS solubility curve applied to oxygen-free system. Typical literature values of metal sulfide solubilities are generally reported at saturated S_T values which have lower solubilities than at unsaturated S_T values. Figure 7 shows the solubilities of several metal sulfides in distilled water at various pH values.

The solubilities of metal hydroxides are also calculated and shown in Figure 7 for comparison purpose. The solubilities of metal hydroxides are considerably higher than those of corresponding metal sulfides except for very high pH values. Almost no metal hydroxide forms at pH less than 6. Besides, the precipitation of metal hydroxides occur only within a narrow pH range. Large difference in solubilities between sulfides and hydroxides can also be examined by comparing the solubility products (Table 4), the K_{sp} values for metal sulfides are considerably smaller than those for metal hydroxides.

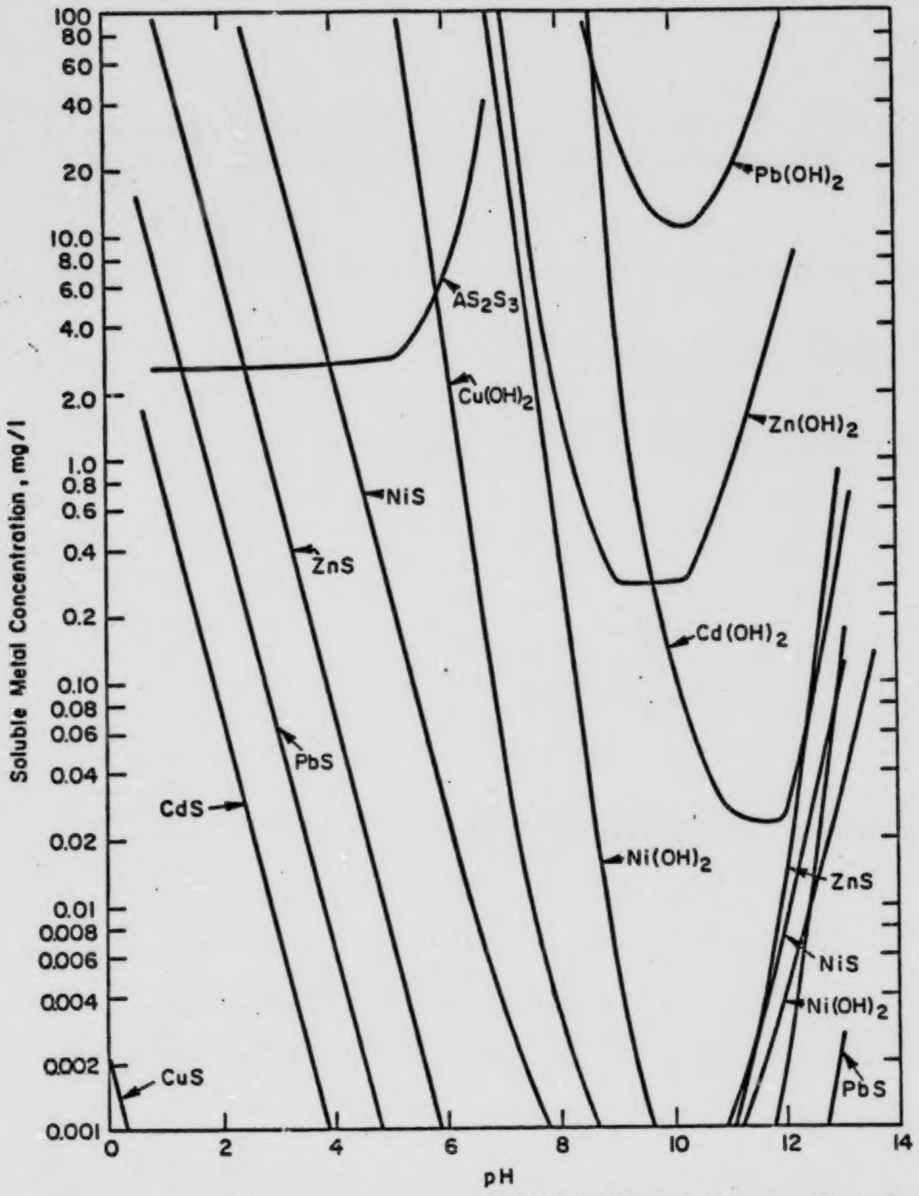

Figure 7. Comparison of the Solubilities Between Metal Sulfides and Metal Hydroxides at Various pH Values.

TABLE 4. COMPARISON OF SOLUBILITY PRODUCT CONSTANTS

Metal Ions	Log Ksp of Metal Sulfide(20)	Log Ksp of Metal Hydroxide(21)
Hg^{2+}	- 52.4	- 52.4
Ag^{+}	- 49.7	- 7.71
Cu^{+}	- 48.0	-------
Cu^{2+}	- 35.1	- 20.4
Cd^{2+}	- 27.7	- 14.4
Pb^{2+}	- 27.0	- 15.3
Zn^{2+}	- 23.8	- 16.7
Ni^{2+}	- 20.7	- 17.2
Fe^{2+}	- 17.3	- 15.2

METAL-SULFIDE-CHELATING AGENT REACTION

Reaction Chemistry

It is well-known that in the presence of chelating agents, hydroxide precipitation of heavy metals is not possible even at high pH values. Sulfide precipitation is shown to be an effective method to remove heavy metals. But the extent of sulfide precipitation is highly influenced by the presence of chelating agents mainly from the competition between the formation of metal sulfide and metal chelates. Five categories of reactions occur in a metal-sulfide-chelating agent system: precipitation of metal sulfide, protonation of sulfide, complexation of metal ion with chelating agents, complexation of metal ion with hydroxide ion, and protonation of chelating agents. An overall reaction schematic diagram is shown in Figure 8.

For chelating agents forming only 1:1 type chelates with metal ions, such as EDTA, equilibrium and stepwise equilibrium constants can be represented by following expressions:

Precipitation of Metal Sulfide:

$$M + S \rightleftharpoons MS_{(s)} \qquad K_{sp} = [M][S] \qquad (23)$$

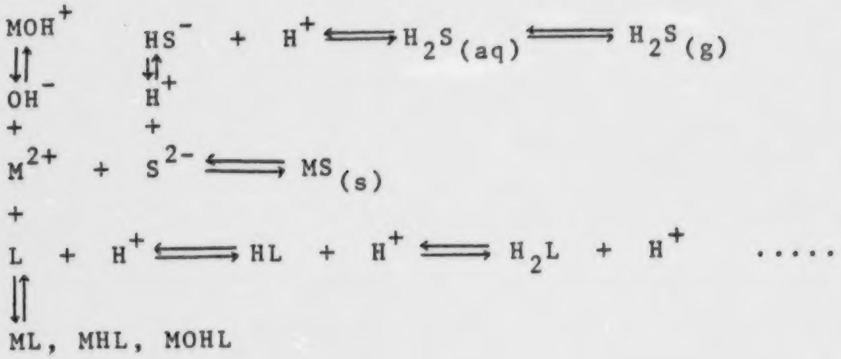
MOH⁺
OH⁻
HS⁻ + H⁺ ⇌ H₂S(aq) ⇌ H₂S(g)
H⁺
M²⁺ + S²⁻ ⇌ MS(s)
L + H⁺ ⇌ HL + H⁺ ⇌ H₂L + H⁺ .....
ML, MHL, MOHL

Figure 8. Reactions for Metal-Sulfide-Chelating Agent System.

Protonation of sulfide ions:

$$S + H \rightleftarrows HS \qquad K_1 = [HS]/[H][S] \qquad (24)$$

$$HS + H \rightleftarrows H_2S \qquad K_2 = [H_2S]/[HS][S] \qquad (25)$$

Complexation of metal ion with chelating agent:

$$M + L \rightleftarrows ML \qquad K_3 = [ML]/[M][L] \qquad (26)$$

$$ML + H \rightleftarrows MHL \qquad K_4 = [MHL]/[ML][H] \qquad (27)$$

$$ML + OH \rightleftarrows MOHL \qquad K_5 = [MOHL]/[ML][OH] \qquad (28)$$

Complexation of metal ion with hydroxide ion:

$$M + OH \rightleftarrows MOH \qquad K_6 = [MOH]/[M][OH] \qquad (29)$$

$$MOH + OH \rightleftarrows M(OH)_2 \qquad K_7 = [M(OH)_2]/[MOH][OH] \qquad (30)$$

$$M(OH)_2 + OH \rightleftarrows M(OH)_3 \qquad K_8 = [M(OH)_3]/[M(OH)_2][OH] \qquad (31)$$

$$M(OH)_3 + OH \rightleftarrows M(OH)_4 \qquad K_9 = [M(OH)_4]/[M(OH)_3][OH] \qquad (32)$$

Protonation of chelating agent:

$$L + H \rightleftharpoons HL \qquad K_{10} = [HL] / [H][L] \tag{33}$$

$$HL + H \rightleftharpoons H_2L \qquad K_{11} = [H_2L] / [HL][H] \tag{34}$$

$$H_2L + H \rightleftharpoons H_3L \qquad K_{12} = [H_3L] / [H_2L][H] \tag{35}$$

$$H_3L + H \rightleftharpoons H_4L \qquad K_{13} = [H_4L] / [H_3L][H] \tag{36}$$

where K_i's are equilibrium constants characterizing the formation of the different species in the solution.

By successive substitution, following relationship can be obtained:

$$HS = K_1 [H][S] \tag{37}$$

$$H_2S = K_1K_2 [H]^2 [S] \tag{38}$$

$$ML = K_3 [M][L] \tag{39}$$

$$MHL = K_3K_4 [M][H][L] \tag{40}$$

$$MOHL = K_3K_5 [M][OH][L] \tag{41}$$

$$MOH = K_6 [M][OH] \tag{42}$$

$$M(OH)_2 = K_6K_7 [M][OH]^2 \tag{43}$$

$$M(OH)_3 = K_6K_7K_8 [M][OH]^3 \tag{44}$$

$$M(OH)_4 = K_6K_7K_8K_9 [M][OH]^4 \tag{45}$$

$$HL = K_{10} [H][L] \tag{46}$$

$$H_2L = K_{10}K_{11}[H]^2\ L \qquad (47)$$

$$H_3L = K_{10}K_{11}K_{12}[H]^3\ L \qquad (48)$$

$$H_4L = K_{10}K_{11}K_{12}K_{13}[H]^4\ L \qquad (49)$$

The residual soluble metal concentration is:

$$C_M = [M] + [ML] + [MHL] + [MOHL] + [MOH] + [M(OH)_2] + [M(OH)_3] + [M(OH)_4] \qquad (50)$$

Total metal presence in the solution is the sum of soluble metal ions, C_M, and metal sulfide precipitate, M_s:

$$M_T = C_M + M_s \qquad (51)$$

Total chelating agent L_T is:

$$L_T = [L] + [HL] + [H_2L] + [H_3L] + [H_4L] + [ML] + [MHL] + [MOHL] \qquad (52)$$

Total sulfide ion S_N is:

$$S_N = [S] + [HS] + [H_2S] + M_s \qquad (53)$$

The equilibrium concentration of all species present in a metal- sulfide-chelating agent system can be calculated by solving a series of simultaneous equations comprising of material balance equations (Equation (31)-(34)), solubility product of metal sulfide defined in Equation (15), expressions of species Equation (37)-(49), pH, total metal concentration, total sulfide concentration, total complexing agent concentration and Table 2. A computer program was designed to solve these equations and calculate the equilibrium concentration of all species.

Metal-Sulfide-Chelating Agent Equilibrium Calculations

Using the calculation procedure described above, the theoretical values of residual metal concentrations, C_M, are calculated for various Zn-sulfide-chelating agent systems at a sulfide dosage of 1.0x and 8.9×10^{-3}M chelating agent concentration and plotted as a function of pH in Figure 9. Zn residual concentrations are always higher in the presence of chelating agents. This indicates that the formation of Zn chelates reduced the extent of ZnS precipitation. For example, at pH 8, zinc residual concentration is about 7mg/l in the presence of the strong chelating agent EDTA while residual concentration is about 10^{-5}mg/l without any chelating agents present. Figure 9 also shows the residual Zn concentrations in the presence of other chelating agents of

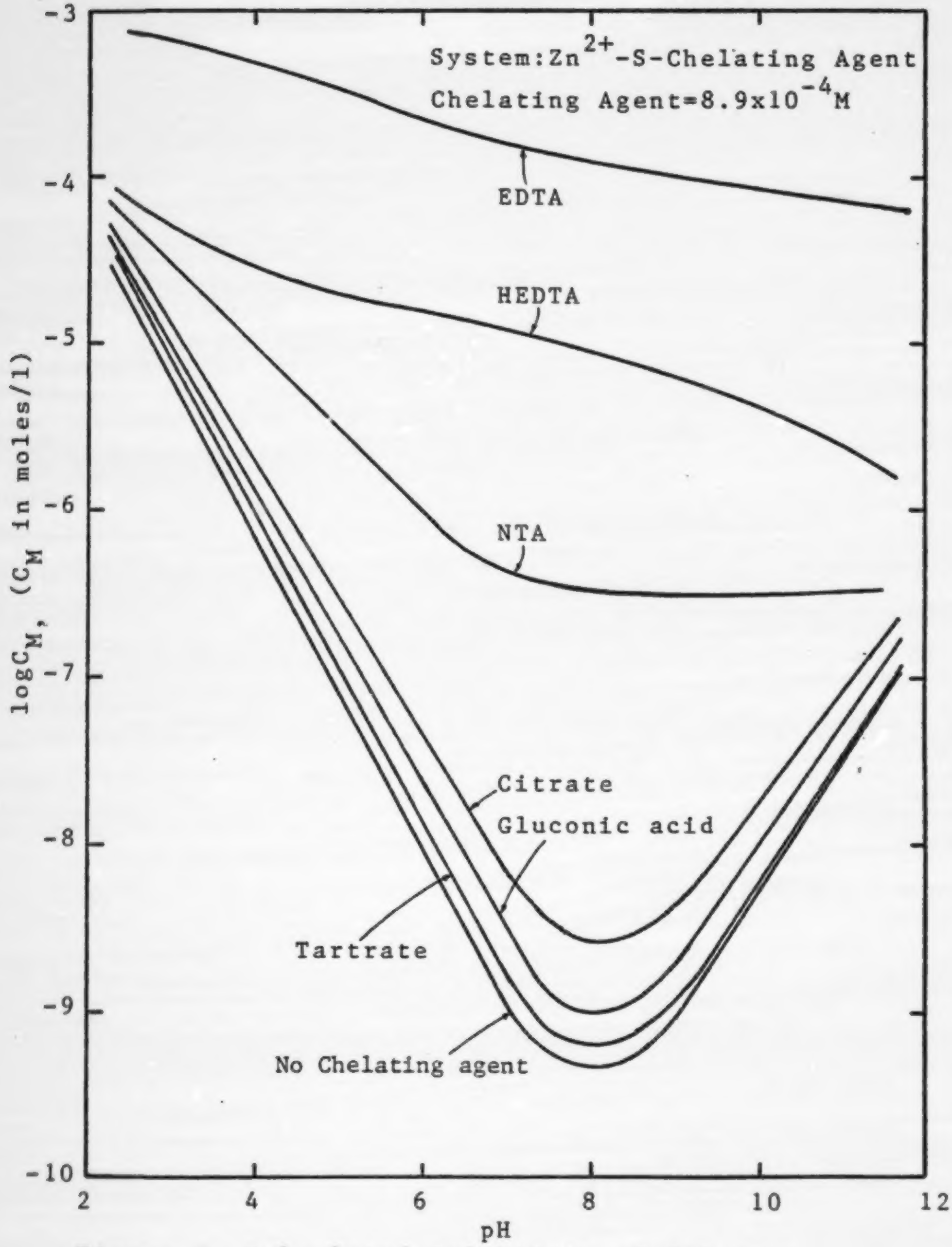

Figure 9. Calculated Solubility of ZnS as a Function of pH in the Presence of Various Chelating Agents.

various degrees of metal chelate stability. Weak chelating agents such as tartrate and gluconic acid show little influence on the residual concentration. The interference of these chelating agents, in terms of reduction of sulfide precipitation, increases in order of : tartrate $<$ gluconic acid $<$ citrate $<$ NTA (nitroloacetic acid) $<$ HEDTA (hydroxyethyl-ethyine-diaimetriacetic acid) $<$ EDTA.

Figure 9 also shows the pH effect on the residual zinc concentration with K_{sp} values shown in Table 3. At low pH, removal of zinc is not complete because the protonation of sulfide tends to form H_2S, and part of H_2S may be lost into air, thus decreasing the extent of ZnS precipitation. In alkaline conditions, metal forms stable chelates because of the deprotonation of chelating agent. For pH 10, formation of metal hydroxide chelates becomes another competing reaction in the presence of some weak chelating agents , and increases residual concentration. But with strong chelating agents, no significant residual change occurs even at high pH because of the formation of highly stable chelates.

The effect of soluble sulfide concentration (S_T) on sulfide precipitation is shown in Figure 10. At higher S_T, the residual concentrations are always lowered. S_T value increases as sulfide dosage exceeds 1.0x. The effect of sulfide dosage is shown in Figure 11, higher dosage of sulfide always lowers the residual metal

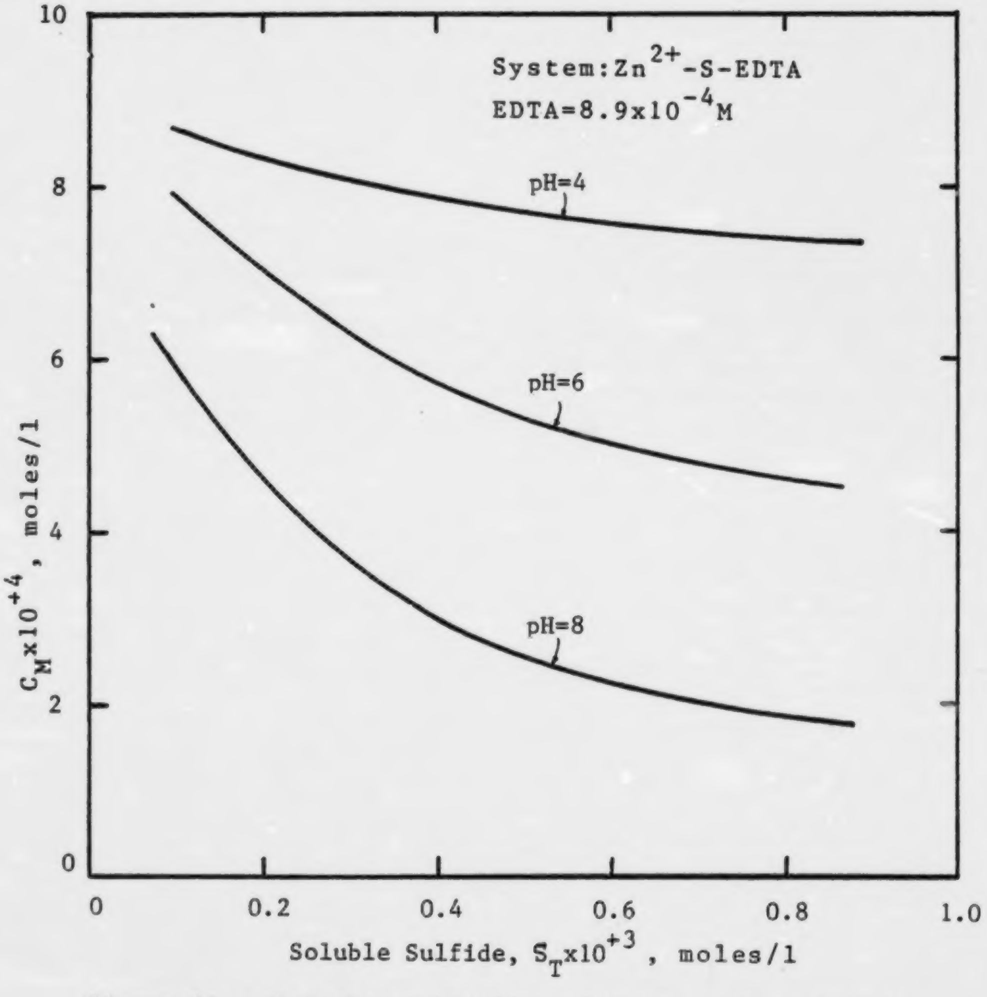

Figure 10. Calculated Solubility of ZnS as a Function of Soluble Sulfide Concentration in the Presence of EDTA.

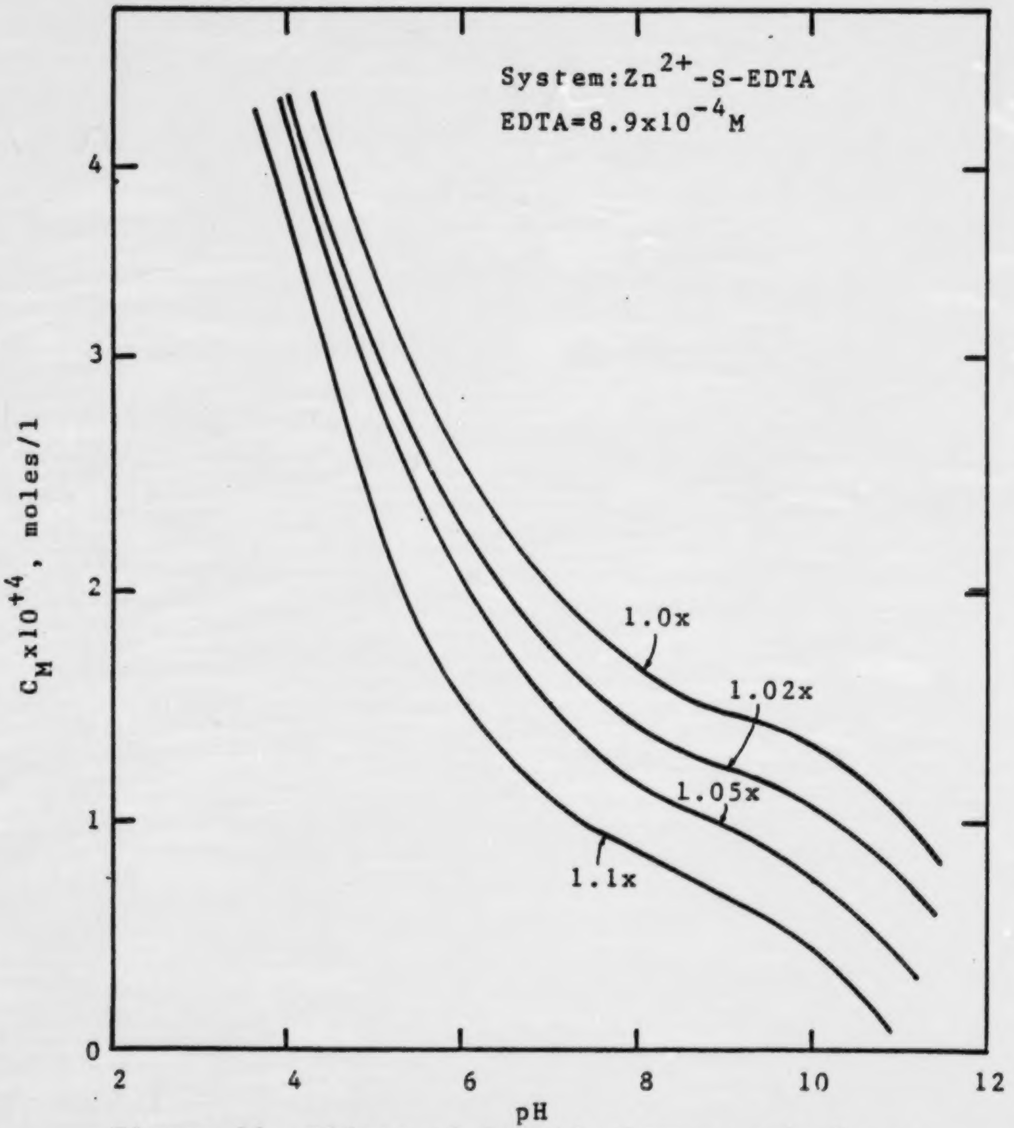

Figure 11. Effect of Sulfide Dosage and pH on Calculated ZnS Solubility in the Presence of EDTA.

concentration due to common ion effect.

Increased concentration of chelating agent present tends to form more metal chelates, thus decreasing metal sulfide precipitation. Figure 12 shows the effect on Zn with various concentration of EDTA.

The results of equilibrium calculations for Cu, Cd and Ni sulfide precipitation are shown in Figure 13, 14 and 15 in the presence of various chelating agents. Because of the high reactivity of Cu with sulfide ($K_{sp} = 1.2 \times 10^{-35}$), the formation of CuS is more favorable over the formation of copper chelates. The effect of the formation of metal-EDTA chelates on various metal sulfide precipitation is plotted in Figure 16. Metal sulfides with small solubility product (K_{sp}), such as Cu and Cd, always have low residual concentrations and are less influenced by the presence of chelating agents.

Comparison with Hydroxide Precipitation

The residual metal concentrations after hydroxide precipitation with EDTA are presented in Figure 16 for several heavy metals. The results are considerably higher for most hydroxide precipitation than for sulfide precipitation, especially at low pH values. For example, at pH 6, Zn does not form hydroxide precipitate while residual is about 16mg/l after sulfide precipitation. The difference is even greater for

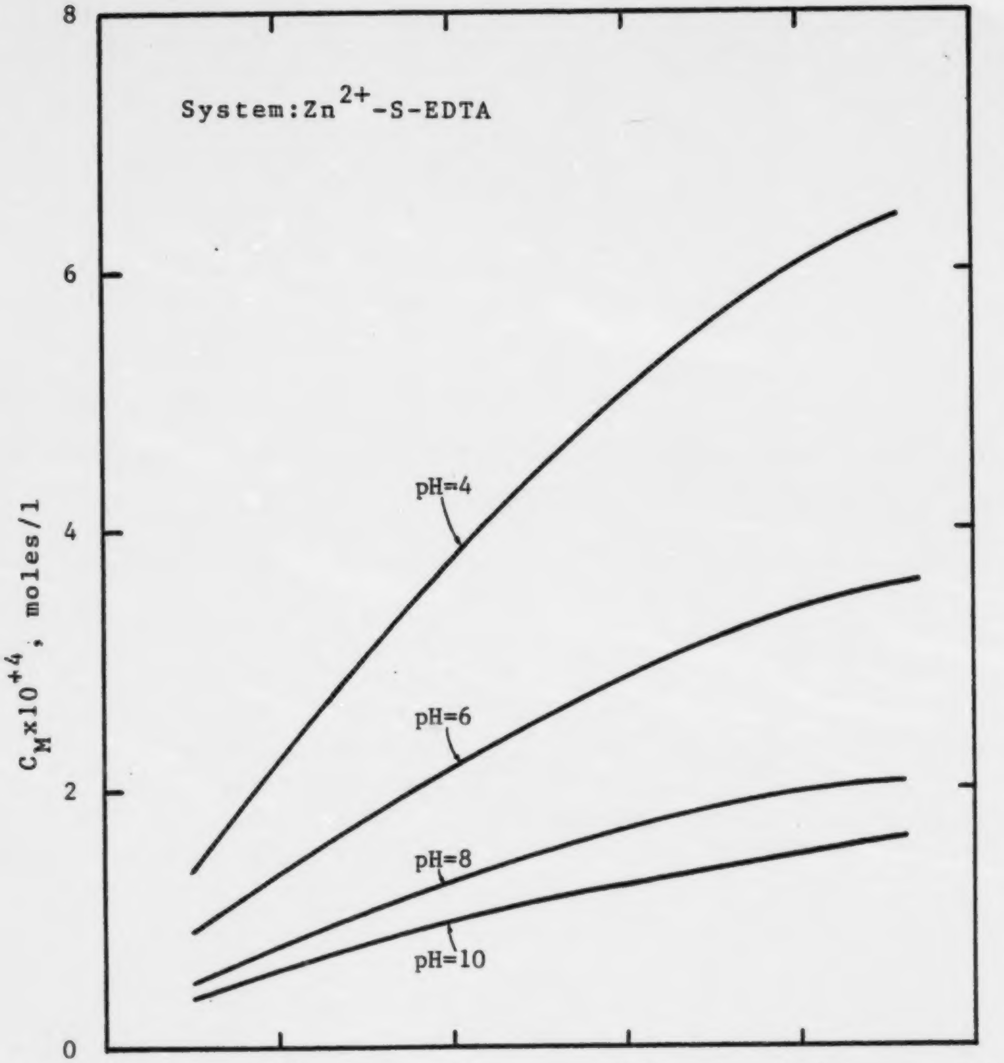

Figure 12. Calculated Solubility of ZnS as a Function of EDTA Concentration for Various pH Values.

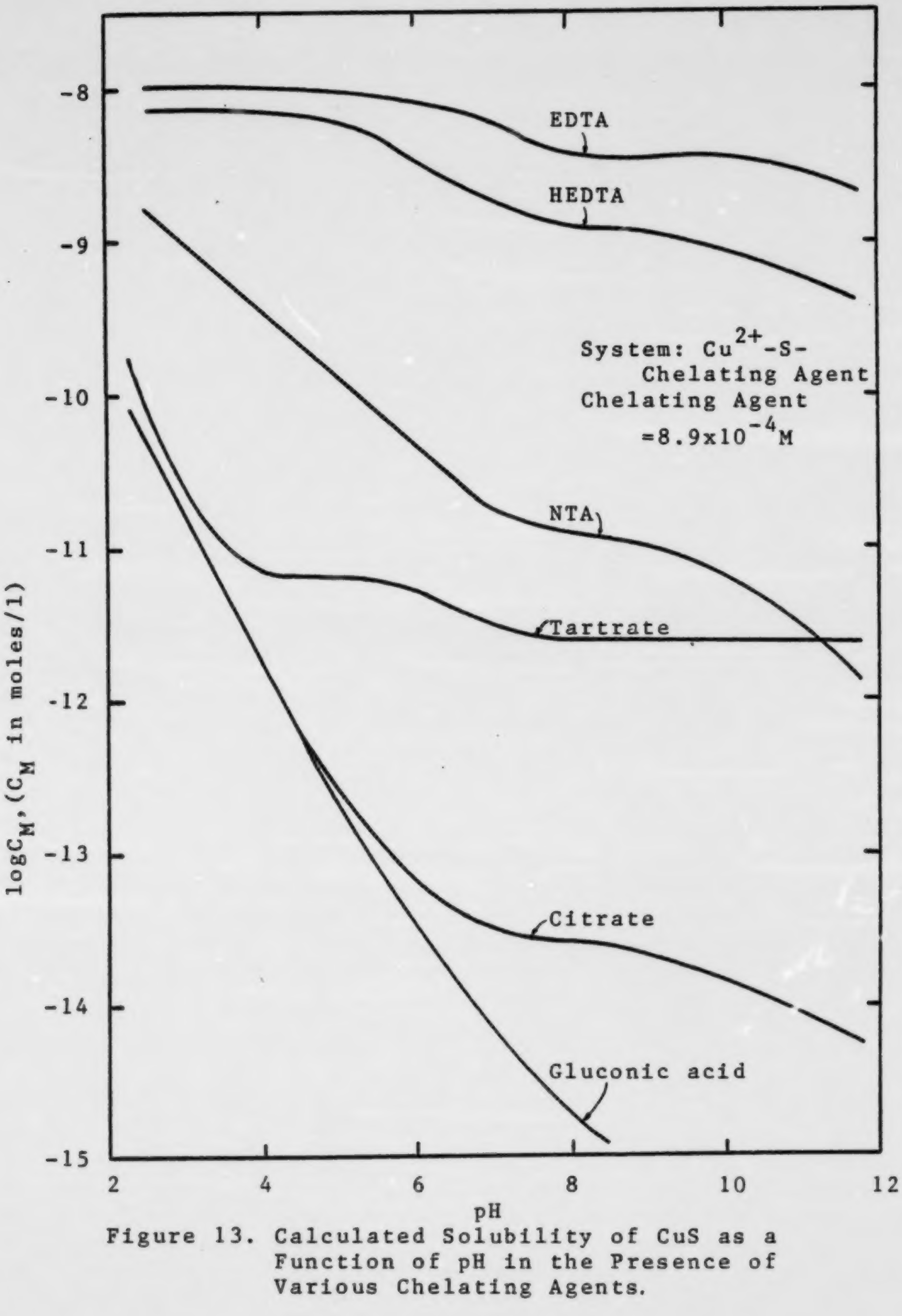

Figure 13. Calculated Solubility of CuS as a Function of pH in the Presence of Various Chelating Agents.

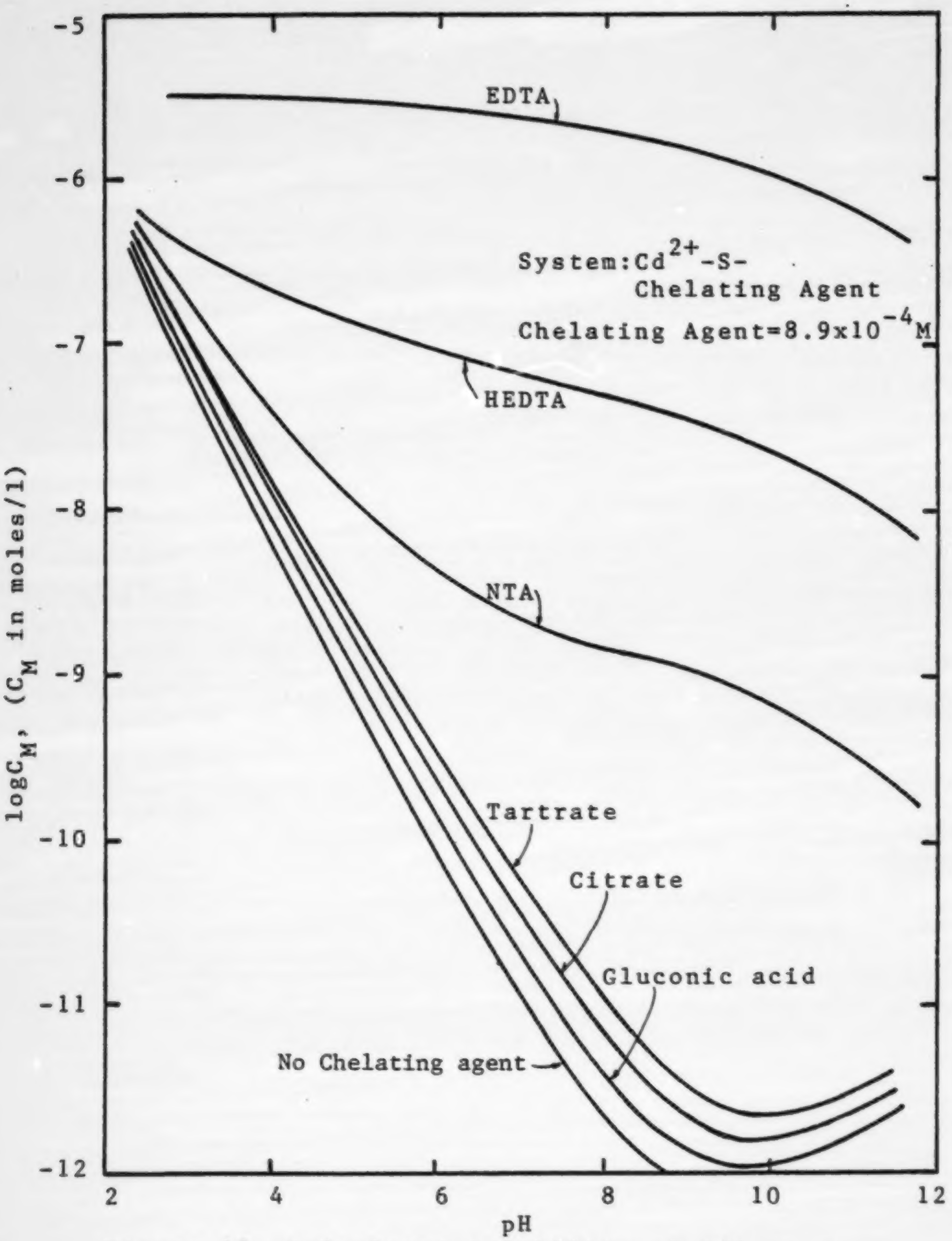

Figure 14. Calculated Solubility of CdS as a Function of pH in the Presence of Various Chelating agents.

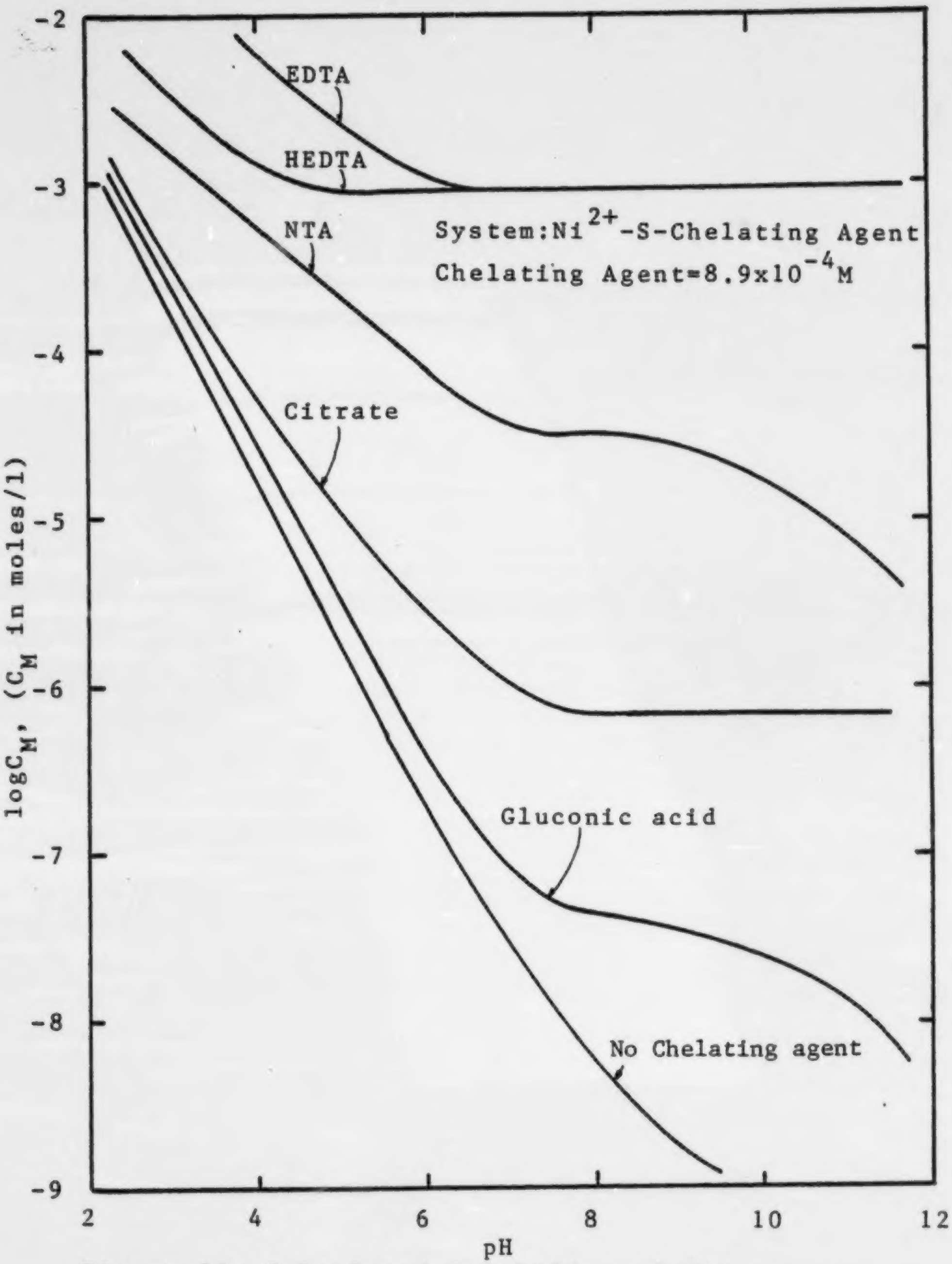

Figure 15. Calculated Solubility of NiS as a Function of pH in the Presence of Various Chelating Agents.

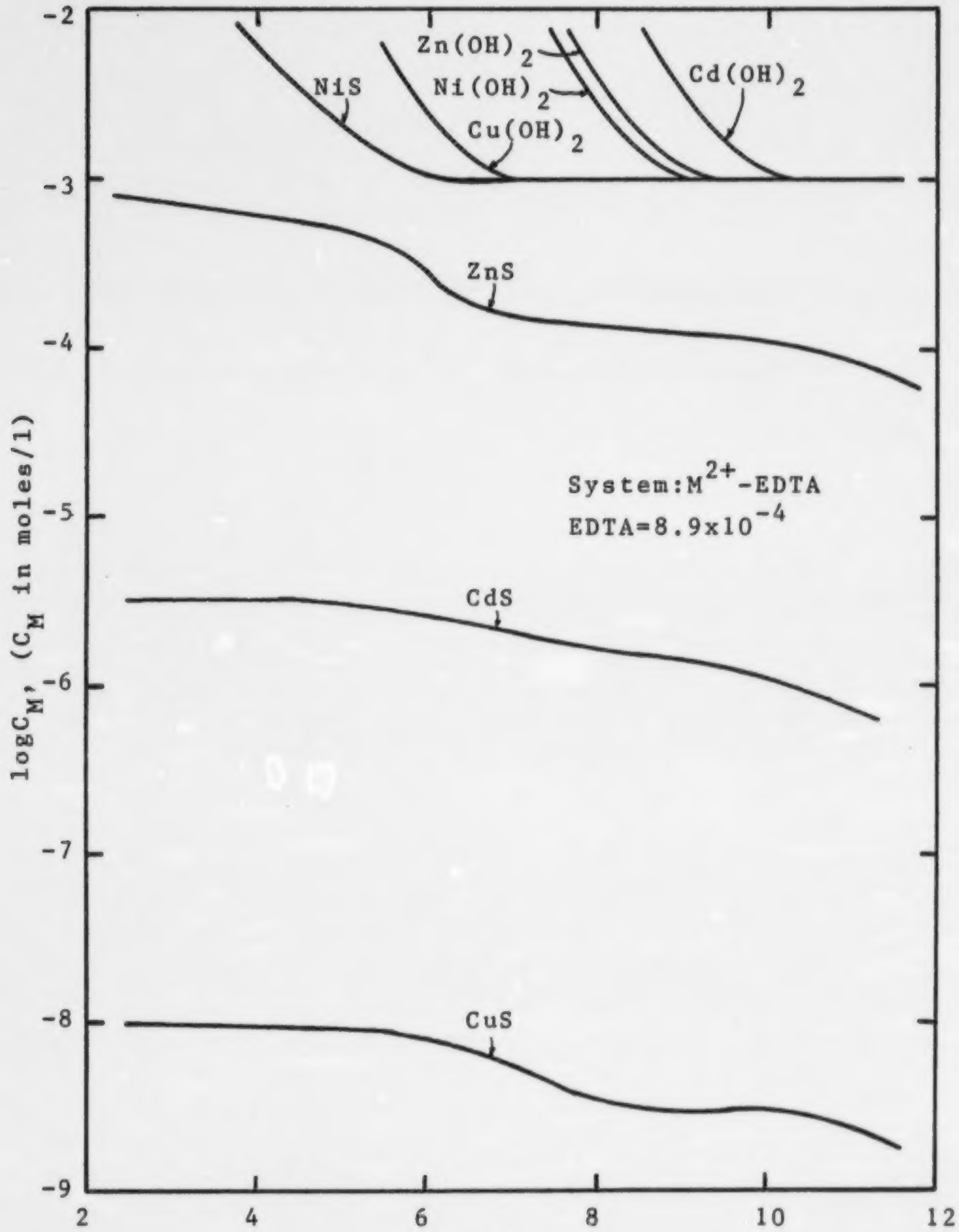

Figure 16. Comparison of Sulfide and Hydroxide Solubilities as a Function of pH in the Presence of EDTA.

Cu and Cd. But for Ni, the formation of Ni-EDTA chelates at high EDTA concentration is more favorable than the precipitation of NiS and thus insignificant precipitation will result.

The residual zinc concentrations for hydroxide precipitation in the presence of various chelating agents are shown in Figure 17 as a function of pH. The precipitation of zinc hydroxide is not influenced by the presence of some weak chelating agents. But the presence of strong chelating agents (such as EDTA) severely decrease the effectiveness of zinc hydroxide precipitation.

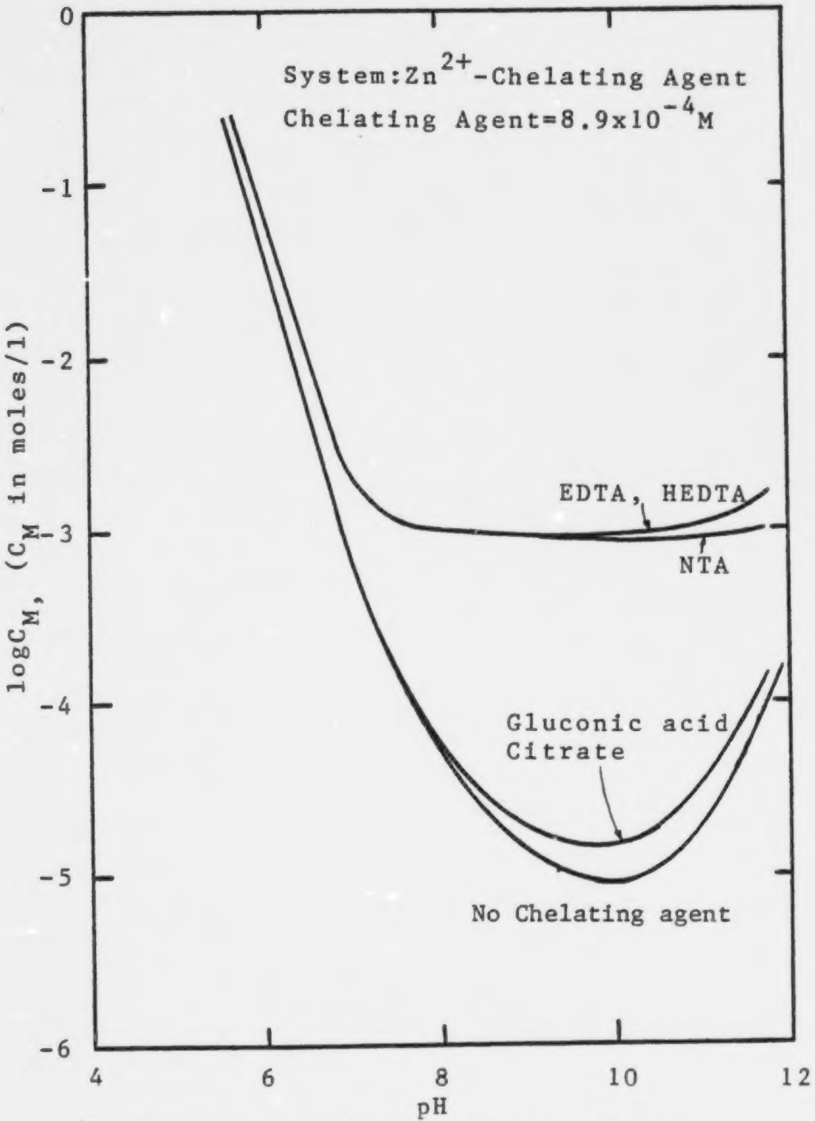

Figure 17. Solubility of $Zn(OH)_2$ as a Function of pH in the Presence of Various Chelating Agents.

SECTION 4

EXPERIMENTAL

In this study, sodium sulfide solutions were used to precipitate heavy metal ions. Most experiments were conducted for single-metal, batch-unit systems in the presence of chelating agents. Limited studies were also carried out without chelating agents for comparison purposes. Multi-metal systems and continuous-unit experiments were conducted with and without chelating agents. The operational conditions under investigation are listed in Table 5.

EQUIPMENT

Reactor and Accessory

Batch unit: This unit consisted of a one- or two-liter beaker with a magnetic stirring device, pH electrode and an automatic pH control unit. The schematic diagram of this unit is shown in Figure 18. High mixing speed was always used to ensure completely mixed condition.

TABLE 5. OPERATIONAL CONDITION

Metal	Chelating Agent	Metal Concentration (mg/l)	Chelating Agent Concentration (mg/l)	pH	Na_2S Dosage	Reaction Time (minutes)
Zn	EDTA	10-500	0-570	4-10	0.5-1.2X	5-60
	Citrate	100	0-900	3-10	1.05X	5-60
	Gluconic Acid	100	100	4-8	1.05X	5-60
	Tartrate	100	100	4-8	1.05X	5-60
Cu	EDTA	100-500	0-500	3-10	0-1.2X	5-60
	Citrate	100	100	4-10	1.05X	5-60
	Gluconic Acid	100	100	4-8	1.05X	5-60
	Tartrate	100	100	4-8	1.05X	5-60
Cd	EDTA	100	0-500	4-10	1.05X	5-60
	Citrate	100	100	4-8	1.05X	5-60
	Gluconic Acid	100	100	4-8	1.05X	5-60
	Tartrate	100	100	4-8	1.05X	5-60
Ni	EDTA	100	50-400	4-10	1.05X	5-60
	Citrate	100	100	4-8	1.05X	5-60
	Gluconic Acid	100	100	4-8	1.05X	5-60
	Tartrate	100	100	4-8	1.05X	5-60

TABLE 5. OPERATIONAL CONDITIONS (CONTINUED)

Metal	Chelating Agent	Metal Concentration (mg/1)	Chelating Agent Concentration (mg/1)	pH	Na_2S Dosage	Reaction Time (minutes)
Cu-Zn	EDTA	100-500 each	0-2000	8	1.05X	5-60
Cu-Cd	EDTA	100 each	0-200	8	1.05X	5-60
Ni-Zn	EDTA	100 each	0-200	8	1.05X	5-60
Cd-Zn	EDTA	100 each	0-200	8	1.05X	5-60
Cu-Ni	EDTA	100 each	0-200	8	1.05X	5-60
Cd-Ni	EDTA	13-100 each	0-200	8	0.5-1.3X	5-60
Cd-Cu-Ni-Zn	EDTA	25-500 each	0-4000	8	1.05X	5-60

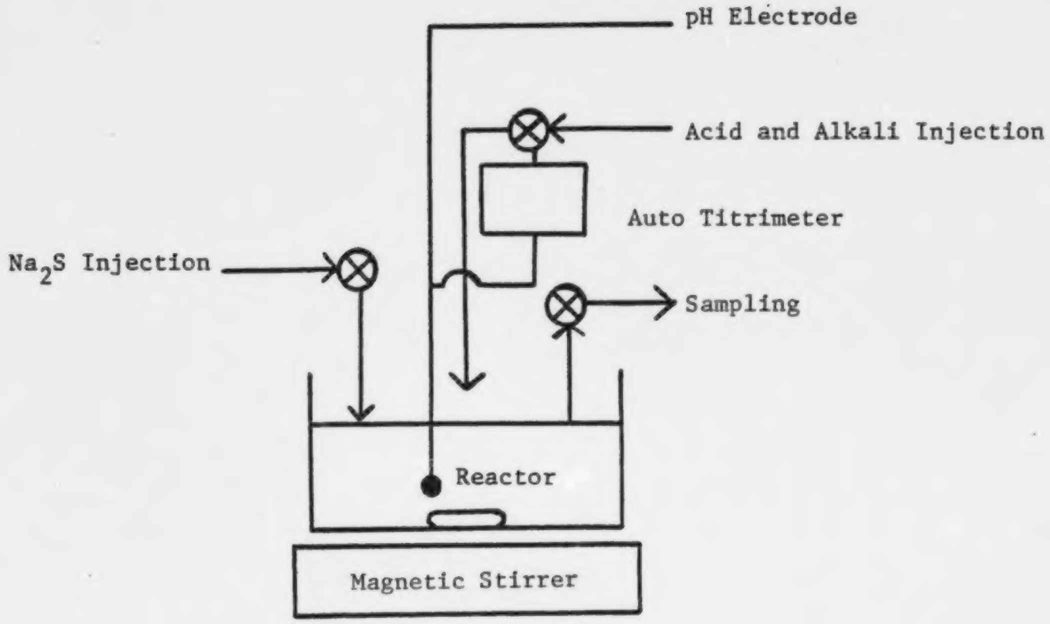
pH Electrode
Acid and Alkali Injection
Auto Titrimeter
Na_2S Injection
Sampling
Reactor
Magnetic Stirrer

Figure 18. Schematic Diagram of Batch Reactor.

Continuous unit: This unit consisted of two one- or two- liter beakers (reactor and a slow-mixing tank) with magnetic stirring devices and pH electrodes. An automatic pH control unit was used in the reactor. A 7-cm diameter and 90-cm high glass column was used as settling column. The schematic diagram of this unit is shown in Figure 19. High mixing speed were used for reactor in order to keep solutions completely mixed and 30-40 rpm of mixing speed were used for slow-mixing tank in order to promote floc growth without breaking up the floc into small pieces.

Filter

A vaccum pump was used for filtration purpose and filters of several different pore sizes (0.45 μm, 0.22 μm, 0.2 μm, 0.1 μm and 0.025 μm) were used in order to examine the particle sizes of various metal sulfides.

Analyzer

Analysis of heavy metals were done by Atomic Absorption. A Varian AA-575 Atomic Absorption Spectroprotometer was used for such purpose. The analytical accuracy was ± 5% and Table 6 lists

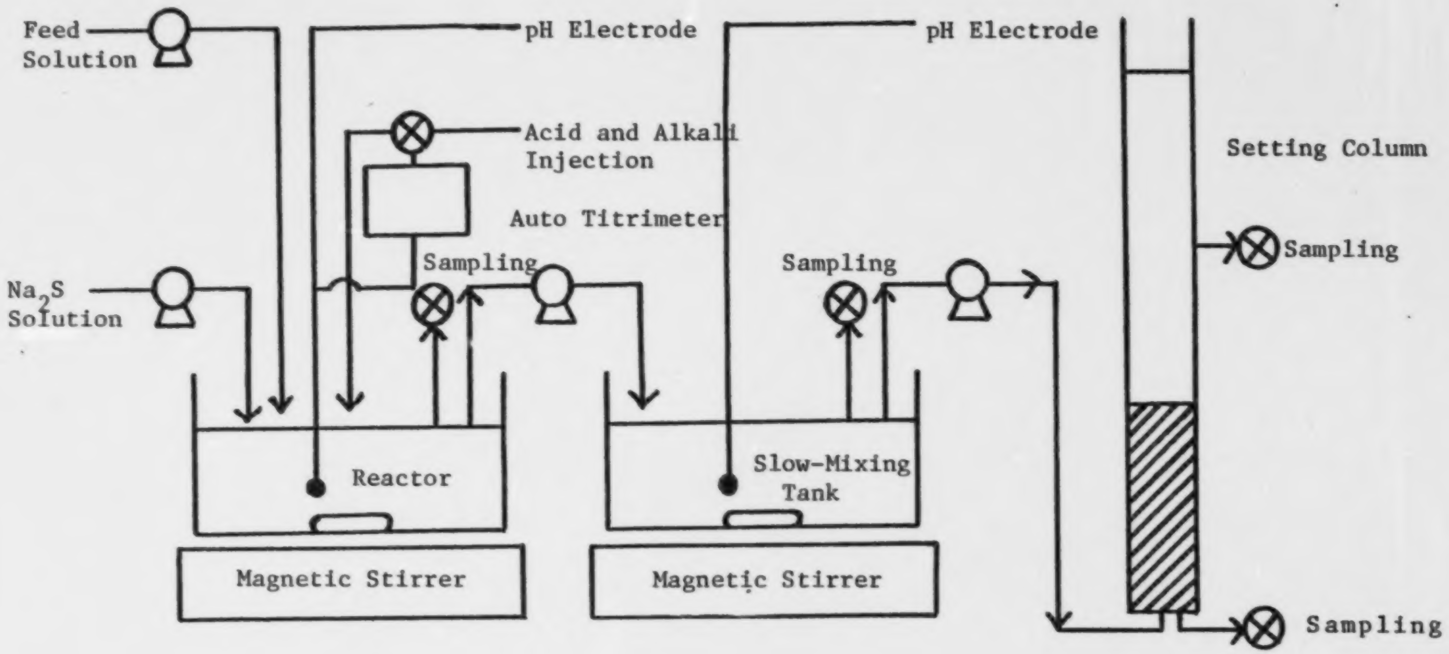
Feed Solution
pH Electrode
pH Electrode
Acid and Alkali Injection
Setting Column
Auto Titrimeter
Sampling
Sampling
Sampling
Na_2S Solution
Reactor
Slow-Mixing Tank
Magnetic Stirrer
Magnetic Stirrer
Sampling

Figure 19. Schematic Diagram of Continuous Unit.

TABLE 6. SENSITIVITY OF METALS OBTAINED WITH VARIAN ATOMIC ABSORPTION SPECTROPHOTOMETER AA-575

Metal Ion	Wavelength (nm)	Sensitivity (mg/l)
Cu^{2+}	324.8	0.04
Ni^{2+}	232.0	0.066
Zn^{2+}	213.9	0.009
Cd^{2+}	228.8	0.011

the principal wavelength and sensitivity for several metals used in this study. pH of the sample solutions were monitered by Corning Model 12 Research pH meters.

CHEMICALS USED

Following analytical reagent grade chemicals were used in this study:

Cadmium sulfate	$3CdSO_4.8H_2O$
Cupric chloride	$CuCl_2.2H_2O$
Cupric sulfate	$CuSO_4.5H_2O$
Nickelous chloride	$NiCl_2.6H_2O$
Zinc sulfate	$ZnSO_4.7H_2O$
Sodium sulfide	$Na_2S.9H_2O$
EDTA disodium salt	$C_{10}H_{14}O_8N_2Na.2H_2O$
Sodium citrate	$C_6H_5O_7Na_3.2H_2O$
Gluconic acid	$C_2H_4O_3$
Sodium tartrate	$C_4H_4O_6Na_2.2H_2O$

Following solution were also used in this study:

5.0 N	H_2SO_4
0.1 N	H_2SO_4
0.1 N	HCl
2.0 N	HNO_3

0.1 N NaOH

5.0 N NaOH

0.1 N Iodine solution

0.01 N Thiosulfate solution

Glacial acetic acid

Starch indicator

PROCEDURE

Preparation of Solutions

Sulfide solution: Known amounts of $Na_2S.9H_2O$ were dissolved in double distilled water. The concentration of sulfide solutions was varied in the range of 0.3 M to 1.2 M. The pH of the solutions were adjusted to slightly basic by adding 0.5 N NaOH in order to avoid $H_2S_{(g)}$ loss. Because of the possible decomposition of Na_2S solution, daily calibration of these stock solutions was conducted.

Calibration of sulfide solution: Direct titration method was used to calibrate the concentration of sulfide solution. Sulfide can be oxidized by iodine as:

$$I_2 + S^{2-} \rightleftharpoons S + 2I^-$$

The reaction is rapid enough for a direct titration (iodine determination). A fixed amount (15-25 ml as X_1) of 0.01 N iodine solution was vigorously mixed with 50-75 ml of double distilled water, drops of 6.0 N NaOH solution were added to maintain basicity. Five ml of the test solution was transferred and added to the mixture. After a few minutes, 1-2 ml of glacial acetic acid was added to acidify this solution. It was titrated with 0.01 N thiosulfate solution (amount of thiosulfate required as X_2 ml) to end point using starch indicator. The total amount (ml) of iodine solution is $I_{total} = X_1 - X_2$. The concentration of sulfide solution could be easily calculated from I_{total}.

Metal solutions: Known amounts of metal salts were dissolved in double distilled water in order to prepare metal solutions. The total metal concentration was varied between 10mg/l to 1000mg/l. If metal-chelating agent solutions were used, known amounts of metal salts were dissolved in a solution containing predetermined quantities of chelating agents. The total chelating agent concentrations were varied in the range of 10mg/l to 4000mg/l.

Experimental Procedure

Batch unit: Figure 18 shows the experimental unit. Metal solution of known concentration (with/without chelating agent) was transferred to reactor beaker. A pH electrode, acid and base injection tube and sulfide injection tube were connected. A magnetic stirring device was used. After initial adjustment of feed solution pH level, a precalculated amount of sulfide solution was added into feed metal solution. With an automatic titrimeter, pH was maintained at desired levels by adding acid or base to the solution. Typical reaction runs took 40 minutes to 2 hours. At various sampling times, a portion of the reaction solution (about 10 ml) was transferred and filtrated immediately. Depending on the metal ions present, different size filter papers were used. The filtrate was analyzed for soluble metals by using atomic absorption spectrophotometry.

Continuous unit: The experimental unit used in this study is shown in Figure 19. Predetermined flowrate of feed metal solution of known concentration (with/without chelating agent) and precalculated flowrate of sulfide solution of 1.05x dosage were pumped into the reactor beaker. An automatic titrimeter was used in the reactor beaker to maintain pH value at some desired levels by adding acid or base for the entire reaction period. Mixing speed was fast for the reactor. Then, the reaction solution was pumped into the slow-mixing tank where mixing speed of about 30 to 40 rpm was used for the growth of particles. Finally, the reaction solution was pumped into settling column for sedimentation. The flowrates of feed solution pumped depended on the detention time needed which varied from 5 minutes to 40 minutes. Typical reaction runs took 2 to 3 hours. Samples were taken at the outlets of reactor, slow-mixing tank and settling column. Both unfiltered and filtered sample solutions were analyzed for metal ions by using atomic absorption spectrophotometry.

SECTION 5

RESULTS AND DISCUSSIONS

For sulfide precipitation, sulfur compound can be added as Na_2S, NaHS or $H_2S_{(g)}$. In this study, all sulfide precipitation experiments were conducted with sodium sulfide solutions. Experiments were generally conducted in an open system unless otherwise specified. The separations achieved are reported in terms of residual metal concentration; the residual metal concentrations were obtained by filtering (through 0.025-0.45μm filter paper) the suspension obtained after sulfide precipitation. Thus, the residual metal concentration refers to the soluble unreacted metal concentration.

The extent of metal sulfide precipitation is expected to be a function of temperature, pH value, reaction time, sulfide dosage and the presence of chelating agents (such as EDTA,etc.). In all discussion and figures, "pH" refers to reaction pH.

Various metal-sulfide-chelating agent systems were studied in this research. Extensive studies were investigated with single-metal, batch-unit systems (with and without chelating agents). Limited precipitation studies were also conducted with multi-metals and continuous-unit systems.

Na_2S-WATER SYSTEM

For the precipitation of metal with sulfide, the formation of hydrogen sulfide (H_2S) gas is possible in the case of overdosage. The formation of H_2S is a function of pH value and sulfide concentration. In the presence of heavy metal, H_2S loss (as gas) was found to be negligible even at pH 3. For example, two experiments (at pH 3, 1.0x Na_2S) with Zn^{2+} and Cu^{2+} showed that Na_2S loss was only 1.2% for zinc and 0.3% for copper. Previous study (15) on the dissolution of sodium sulfide showed the addition of sulfide into water elevates pH value to 10-12, depending on the dosage of sulfide. This can be explained by the strong basic character of sulfide ion. The hydrolytic reaction of S^{-2} ion is expressed as follows:

$$S^{2-} + H_2O \rightleftharpoons HS^- + OH^- \tag{54}$$

At very high pH, this reaction is negligible, and S^{2-} ion predominates (Figure 5).

SULFIDE PRECIPITATION OF SOLUTIONS CONTAINING SINGLE HEAVY METAL ION IN THE PRESENCE OF CHELATING AGENTS

Zinc Sulfide Precipitation

The primary reaction of divalent zinc ion to form zinc sulfide is expressed by following expression:

$$Zn^{2+} + S^{2-} \rightleftharpoons ZnS \qquad (55)$$

In the presence of chelating agents, this reaction is interferred because the formation of zinc chelates.

Removals of zinc by precipitation in the presence of various chelating agents have been studied extensively here; similiar experiments were carried out for copper, cadmium and nickel ion for comparison purpose.

Effect of Chelating Agents:

Several experiments were carried out at pH 8.0 and in the presence of various chelating agents. Results are shown in Table 7. Comparing with the cases without any chelating agent present, the residual zinc concentration were found to be higher in the presence of chelating agents. This indicates that the formation of zinc chelates interferred the precipitation of

TABLE 7. EFFECT OF CHELATING AGENTS ON ZnS PRECIPITATION

Zn Concentration = 100 mg/l

Na_2S Dosage = 1.05X

Chelating Agent Concentration = 100 mg/l

Reaction Time = 30 minutes

Chelating Agent	Residual Metal Concentration (mg/l) (0.45 µm filter)	
	pH = 4.0	pH = 8.0
EDTA	16.5	12.8
Citrate	1.8	0.8
Gluconic Acid	---	0.6
Tartrate	---	0.3
No Chelating Agent	0.3	0.2

zinc sulfide to some extent. In this study, EDTA, citrate, tartrate and gluconic acid were used as chelating agents. Among these chelating agents, EDTA has the highest complex formation equilibrium constants which indicates EDTA may form more stable chelates with zinc ion than other chelating agents used in this study. As predicted, experimental results (Table 7) shows a higher residual concentration was obtained in the presence of EDTA. For weak chelating agents such as citrate and tartrate, the sulfide precipitation is quite complete which indicates the formation of zinc chelates with citrate or tartrate is much less favorable than the formation of zinc sulfide precipitation.

According to Le Chatelier's principle of equilibrium, the residual metal concentration increases with an increase in the amount of chelating agent present in initial feed solution. This is verified to be true for zinc-EDTA system. Experiments were conducted at pH 8.0 and in the presence of various amounts of EDTA for zinc-EDTA system. The results are shown in Figure 20. Residual zinc concentration increased with the increasing amount of EDTA present in the solution. High concentration of EDTA caused very severe interference on the precipitation of zinc sulfide. For example, 72mg/l of zinc residual did not precipitate with sulfide in the presence of 500mg/l of EDTA. The slope of the line in Figure 20 is about 0.125. Assumptions can be made

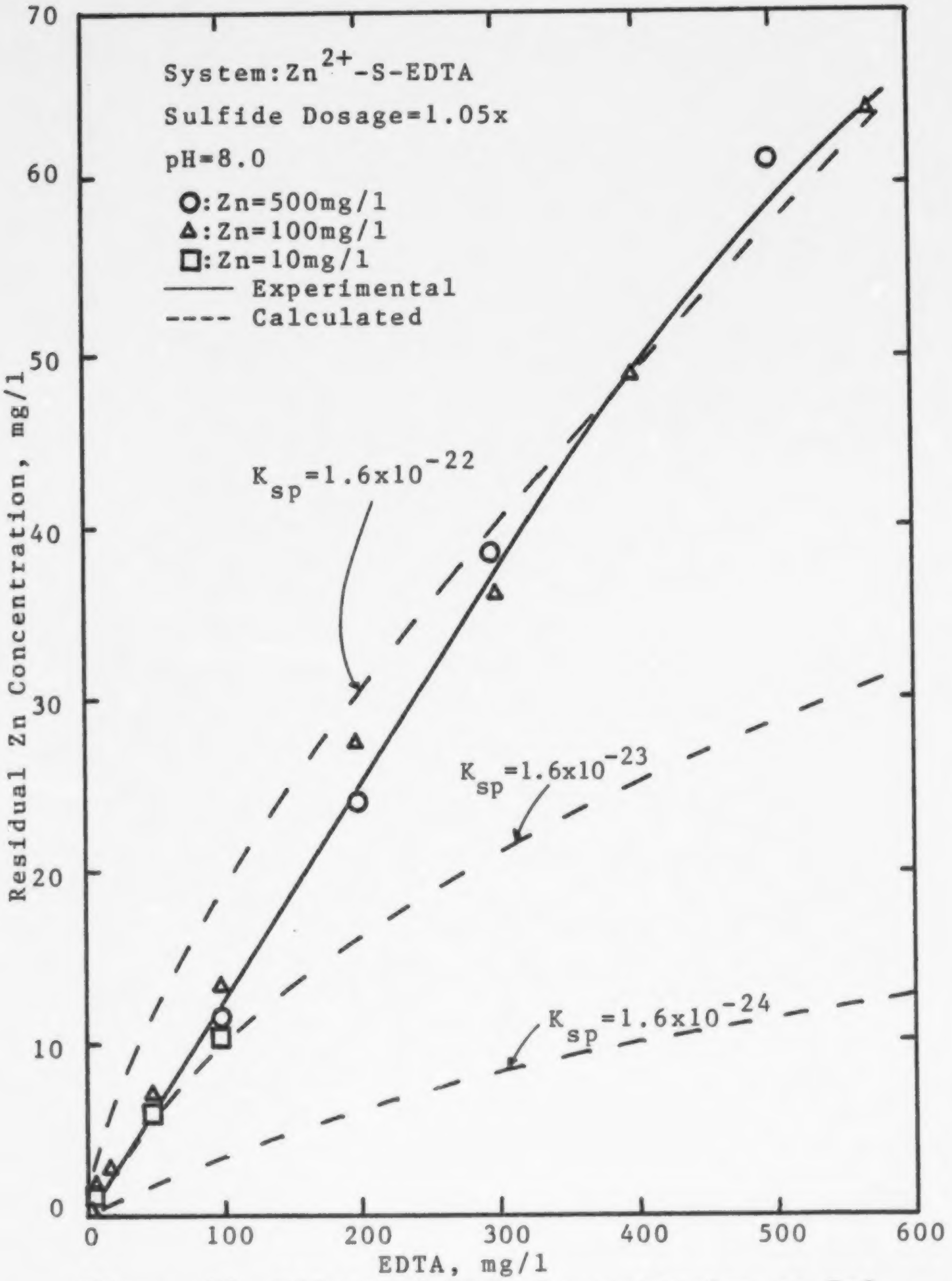

Figure 20. Effect of EDTA Concentration on ZnS Precipitation.

that about 70% of EDTA formed 1:1 chelates with zinc at EDTA less than 500mg/l and EDTA/Zn ratio less than 1.0, that is, about 12.5mg/l of soluble zinc concentration present with 100mg/l of EDTA. This assumption agreed with the fact that almost no precitation occurred when initial zinc concentration equal to 10mg/l and EDTA equal to 100mg/l (3.4×10^{-4}M). Some experiments were carried out for zinc-citrate system. The experimental data are listed in Table 8. Presence of citrate had negligible influence on the precipitation of zinc sulfide. This is because of the weak chelation ability of citrate; sulfide ion competed successfully than citrate for the coordinative positions on the zinc ion.

It should be noted that residual metal concentration at fixed chelating agent concentration should not be affected by the initial concentration of zinc at stoichiometric dosage of sulfide and fixed pH value. This phenomenon was verified to be true for zinc-EDTA system where 10, 100 and 500mg/l of zinc solution were treated by sulfide. The results are also shown in Figure 20 by different symbols for various zinc concentration.

Effect of pH Value:

The species distribution of different forms of metal chelates present in the solution varies at different pH values

TABLE 8. EFFECT OF CITRATE CONCENTRATION ON ZnS PRECIPITATION

Na_2S Dosage = 1.05X

pH = 8.0

Reaction Time = 30 minutes

Initial Zn Concentration (mg/l)	Citrate Concentration (mg/l)	Residual Zn Concentration (mg/l) (0.45 µm filter)
100	0	0.35
100	23	0.60
100	92	0.70
100	225	0.85
200	450	0.75
200	900	0.80

(Figure 3 and 4). In order to evaluate the effect of pH on the removal of metal by sulfide precipitation in the presence of chelating agents, a series of experiments were carried out at 1.05x sulfide dosage and various pH values in the presence of 10 or 100mg/l of EDTA. The residual zinc concentration at various pH values are shown in Figure 21. Removal of zinc by sulfide precipitation was relatively incomplete at pH 3 because of the competion of sulfide ion for H^+. On the other hand, protonated EDTA species, H_4EDTA or H_3EDTA^- are predominant at low pH values, thus competion of metal-EDTA chelates is insignificant and less influential on the residual zinc concentration . As pH value increases, more deprotonated EDTA species such as $HEDTA^{-3}$ or $EDTA^{-4}$ are predominant in the solution. Complexation reaction of metal-EDTA chelates becomes a competing side reaction which tends to increase residual zinc concentration. Figure 21 shows at EDTA concentration less than 10mg/l, the residual zinc is almost independent of pH. For high concentration of EDTA and at pH greater than 8.0, although EDTA forms strong metal-EDTA chelates, the solubility of ZnS precipitate is also lower (see Figure 9) and thus there appears to have a compensating effect on the interference of EDTA.

In the presence of some weak chelating agents, residual metal concentration depends strongly on pH values. Some

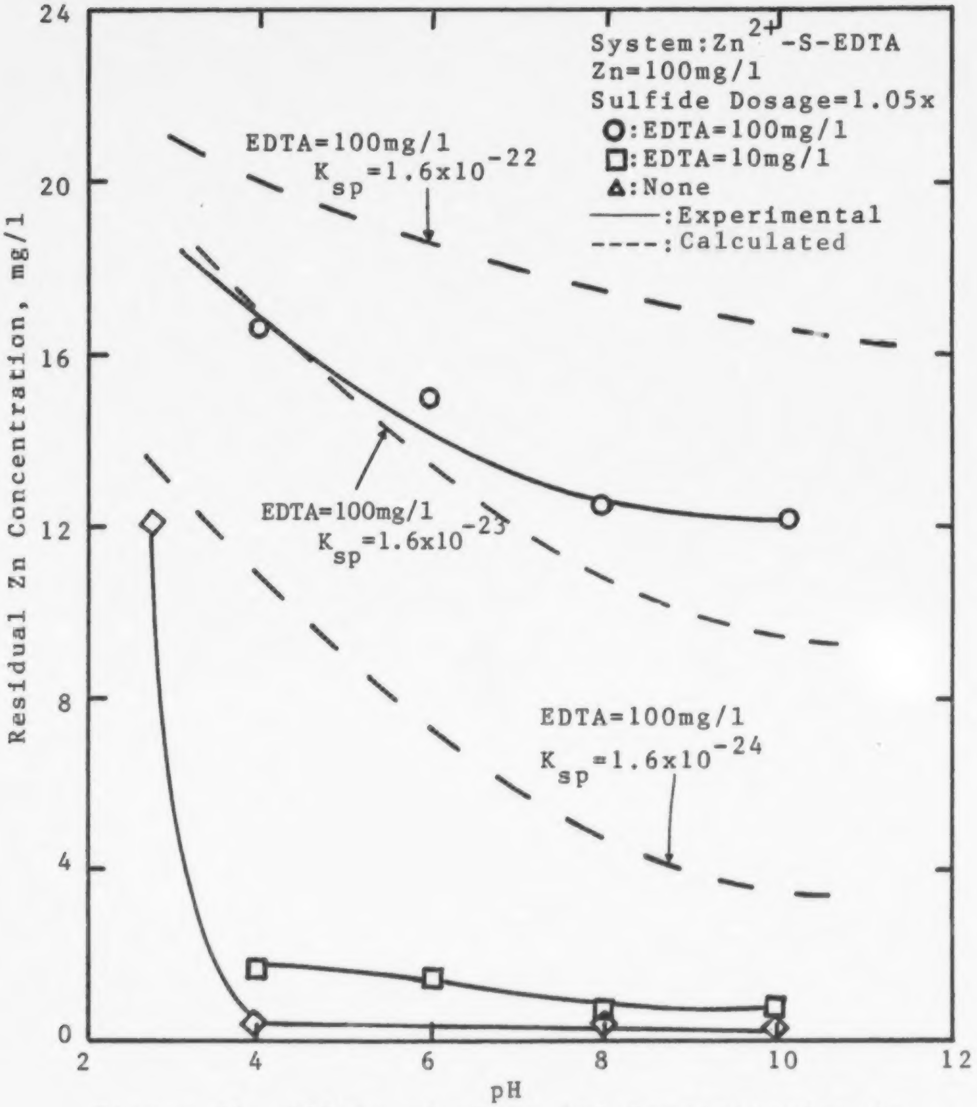

Figure 21. Effect of pH on ZnS Precipitation in the Presence of Various Concentrations of EDTA.

experimental results are shown in Figure 22 for zinc-citrate system. Satisfactory precipitations of zinc sulfide were obtained between pH 4 and 8 in the presence of 100mg/l of citrate. It should be noted that with a weak chelating agents (such as citrate) even at pH 4 , the residual zinc concentration is about 1/8 of that obtained with Zn-EDTA system.

Effect of Sulfide Dosage:

Studies were made at pH 8 with Zn-EDTA system for various sulfide dosages. Theoretically, the soluble zinc concentration should decrease since total soluble sulfide increases at dosage greater than 1.0x (as shown by the calculation in Figure 10). But the experimental results shown in Figure 23 indicates that residual zinc concentration is about 12mg/l and no significant change took place at sulfide dosage greater than 1.0x. This maybe due to the fact that part of excess sulfide was lost to air as $H_2S_{(g)}$. This effect can be verified by the fact that overdosage of sulfide always caused characteristic rotten-egg odor of $H_2S_{(g)}$. The formation of H_2S (by $2H^+ + S^{2-} \rightleftharpoons H_2S$) becomes an important side reaction when sulfide dosage greater than 1.0x is used in sulfide precipitation.

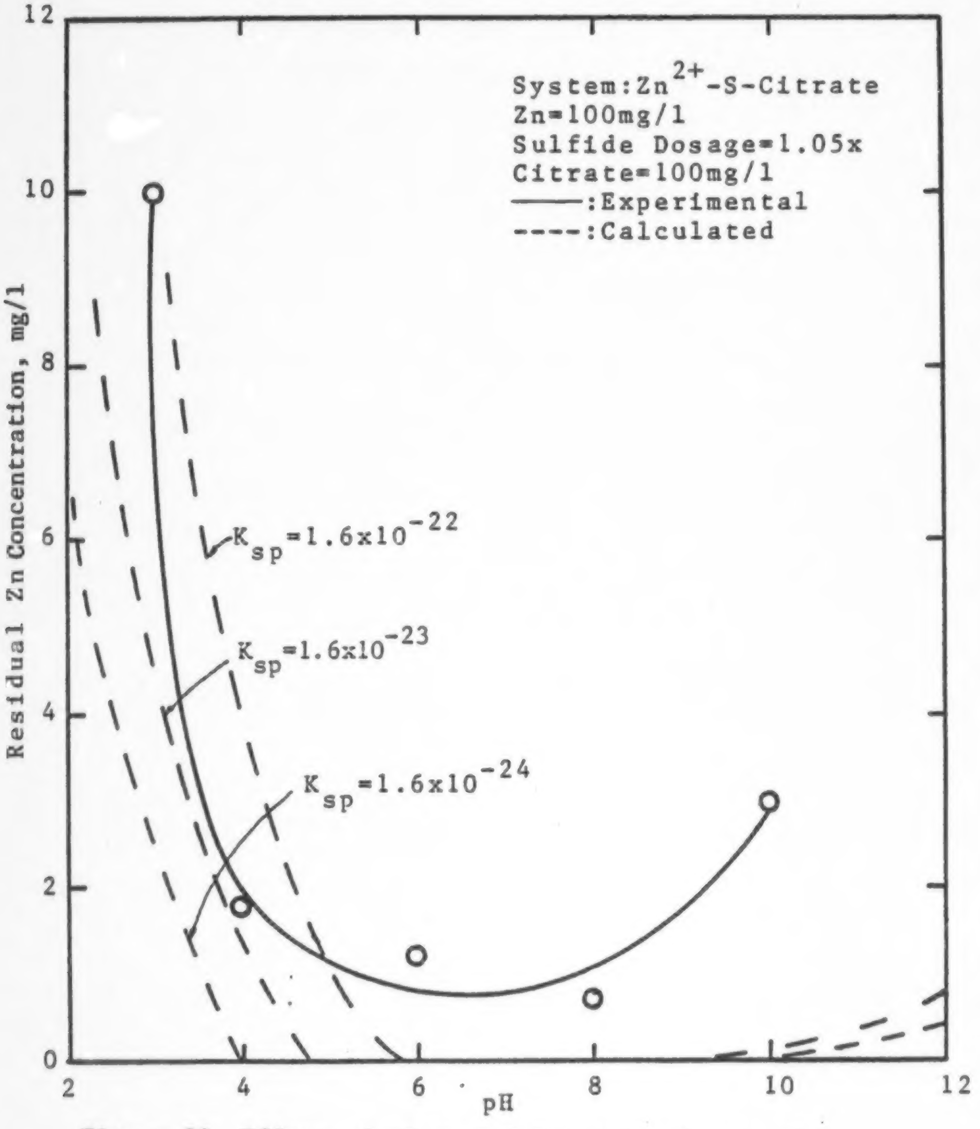

Figure 22. Effect of pH on ZnS Precipitation in the Presence of Citrate.

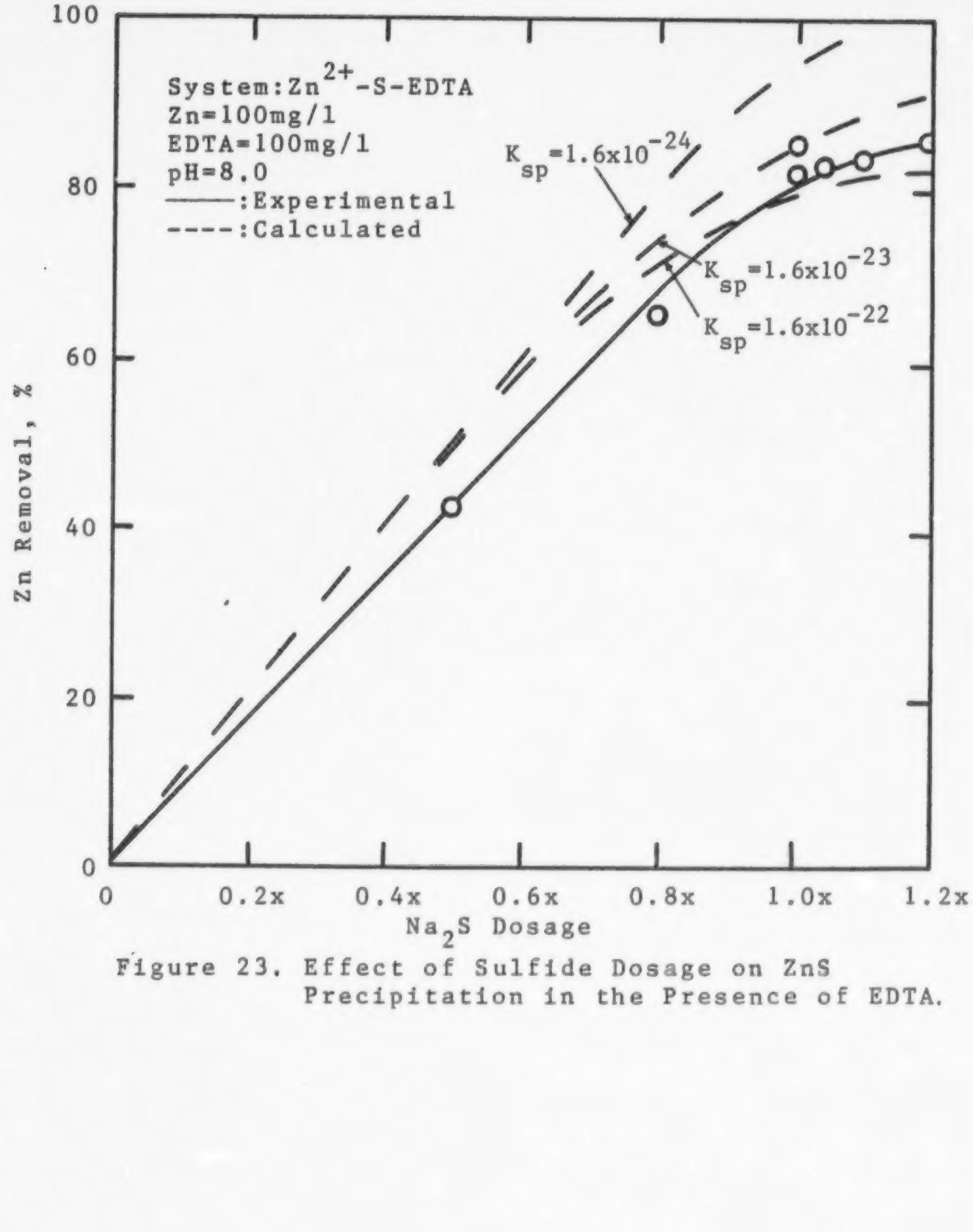

Figure 23. Effect of Sulfide Dosage on ZnS Precipitation in the Presence of EDTA.

Effect of Reaction Time:

In order to find the reaction time effect on zinc sulfide precipitation, experiments were carried out for various zinc-chelating agent systems. Sample solution were taken at various time periods and filtrated for analysis. The results are shown in Figure 24. Zinc sulfide precipitation was very fast and reached equilibrium in a very short time. No significant change in residual zinc concentration was observed after a reaction time of 5 minutes.

Comparison of Experimental Data and Calculated Solubilities

Theoretical zinc solubilities for corresponding experimental conditions were plotted in Figure 20-23 for comparison purpose. Experimental data always show higher residual zinc concentration than values calculated with literature K_{sp} of zinc sulfide. This phenomenon can be explained by the fact that zinc sulfide exists in several polytypic forms (22). The stable forms at room temperature are sphalerite (cubic close packing) and wurtzite (hexagonal close packing) which has different solubility product in water. The values of K_{sp} varies from 10^{-24}(sphalerite) to

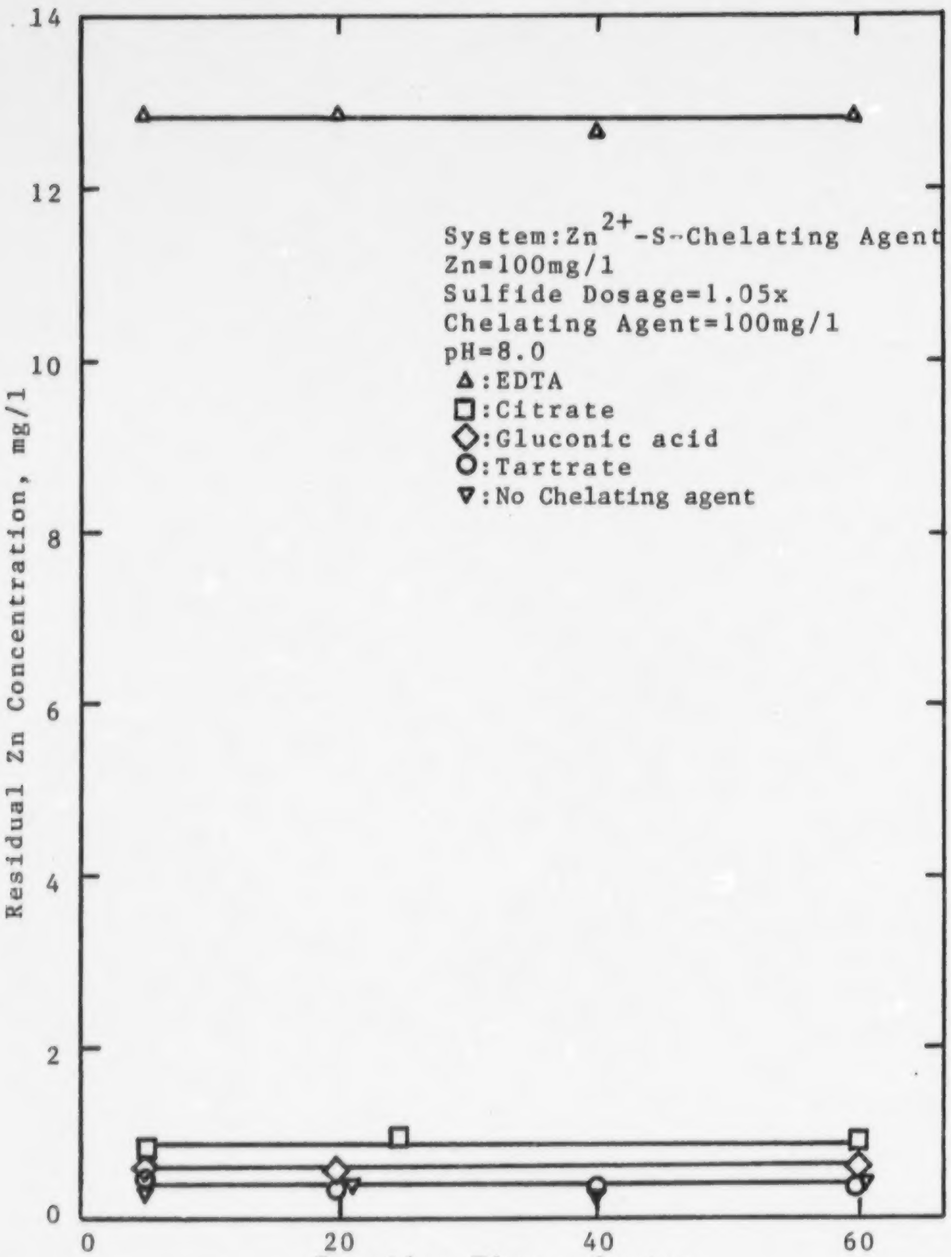

Figure 24. Effect of Reaction Time on ZnS Precipitation in the Presence of Various Chelating Agents.

10^{-22}(wurtzite). The experimental data always fall between the solubilities calculated from these two K_{sp} values indicating that zinc sulfide may exist in both forms when precipitation occurs. Calculated residual zinc concentration for different K_{sp} values are compared and shown by dotted lines in Figures 20-23.

Copper Sulfide Precipitation

A series of experiments were conducted to study the effect of chelating agents on copper sulfide precipitation. The results are shown in Table 9 which indicates that the removal of copper with sulfide precipitation was satisfactory even in the presence of EDTA. For example, at pH 8.0 and EDTA =100mg/l, residual copper concentration was only about 0.6mg/l.

Figure 25 shows the effect of EDTA concentration on residual copper concentration. Higher concentration of EDTA caused more copper residual; about 6% of EDTA formed chelates with copper at pH 8.0, comparing with zinc sulfide, copper sulfide precipitate was much more complete and less influenced by the presence of chelating agents.

TABLE 9. EFFECT OF CHELATING AGENTS ON CuS PRECIPITATION

Cu Concentration = 100 mg/l

Na_2S Dosage = 1.05X

Chelating Agent Concentration = 100 mg/l

Reaction Time = 30 minutes

Chelating Agent	Residual Metal Concentration (mg/l) (0.025 µm filter)	
	pH = 4.0	pH = 8.0
EDTA	0.85	0.7
Citrate	0.65	0.4
Gluconic Acid	0.25	---
Tartrate	0.15	0.1
No Chelating Agent	0.08	<0.05

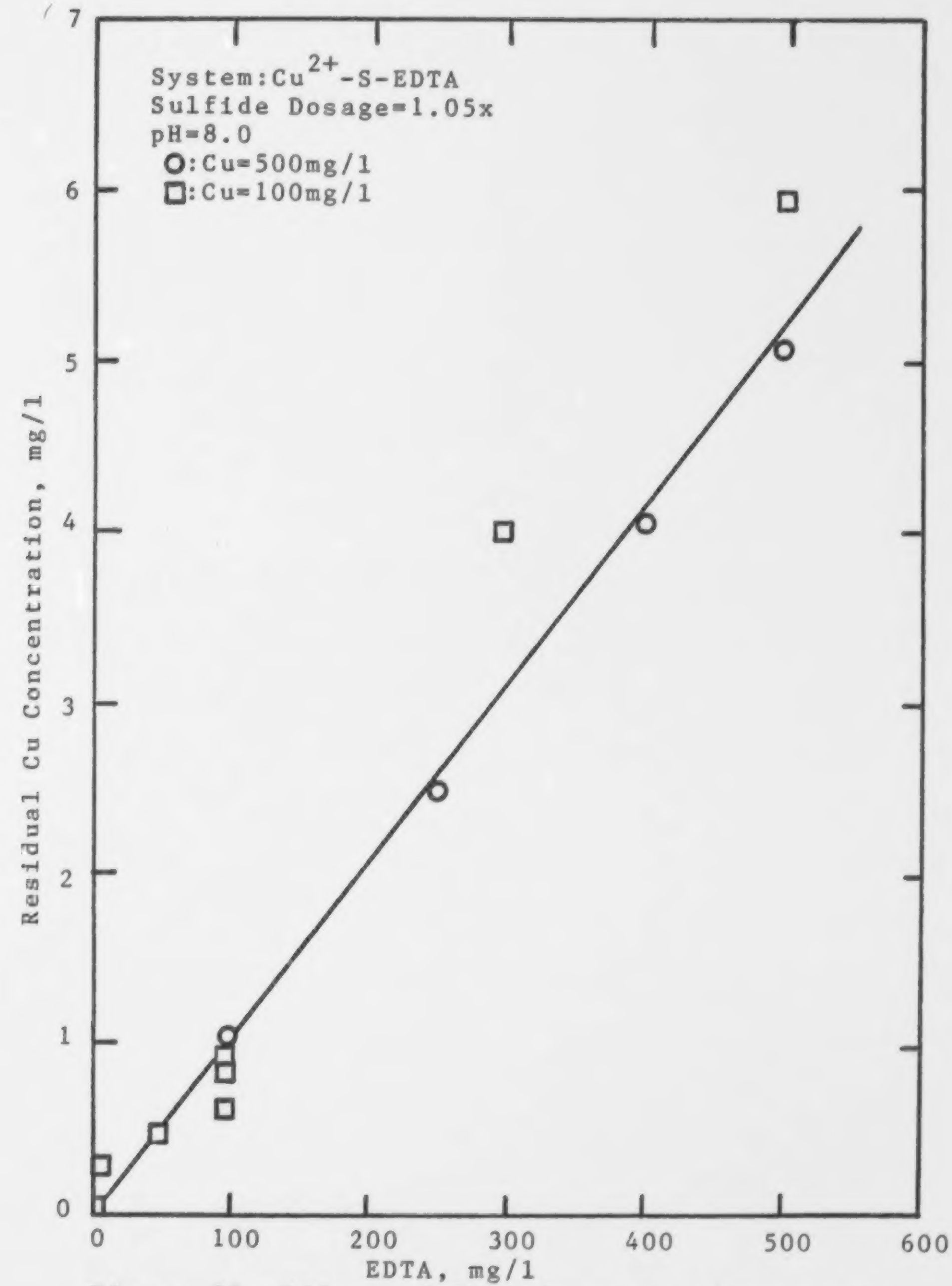

Figure 25. Effect of EDTA Concentration on CuS Precipitation.

The effect of sulfide dosage on residual copper concentration was also studied for various initial concentrations of copper. Figure 26 shows that copper removals were greater than 99% when 1.0x sulfide dosage were used. At sulfide dosage less than 1.0x, the precipitation of copper sulfide agreed with the stoichiometry of sulfide dosage.

Evaluation of pH effect was made with EDTA of 100mg/l and 300mg/l at stoichiometric sulfide dosage. Figure 27 shows that copper removals were complete at pH value between 4 and 8. But it should be noted that even at very low pH (=1.5), the precipitation of copper sulfide was satisfactory. The precipitation of copper sulfide at low pH is further complicated because the formation of Cu_2S. Cu_2S formation involves the following reactions:

$$2Cu^{2+} + S^{2-} \rightleftharpoons 2Cu^{+} + S \qquad (56)$$

$$2Cu^{+} + S^{2-} \rightleftharpoons Cu_2S \qquad (57)$$

the theoretical solubility of Cu_2S is less than CuS indicating that at very low pH, the dissolution of Cu_2S must be taken into account in addition to CuS. Some experiments were conducted for Cu-citrate system and results are shown in Table 10. No significant difference of residual copper concentrations were observed at different pH values, even at low pH 4 or high pH 10.

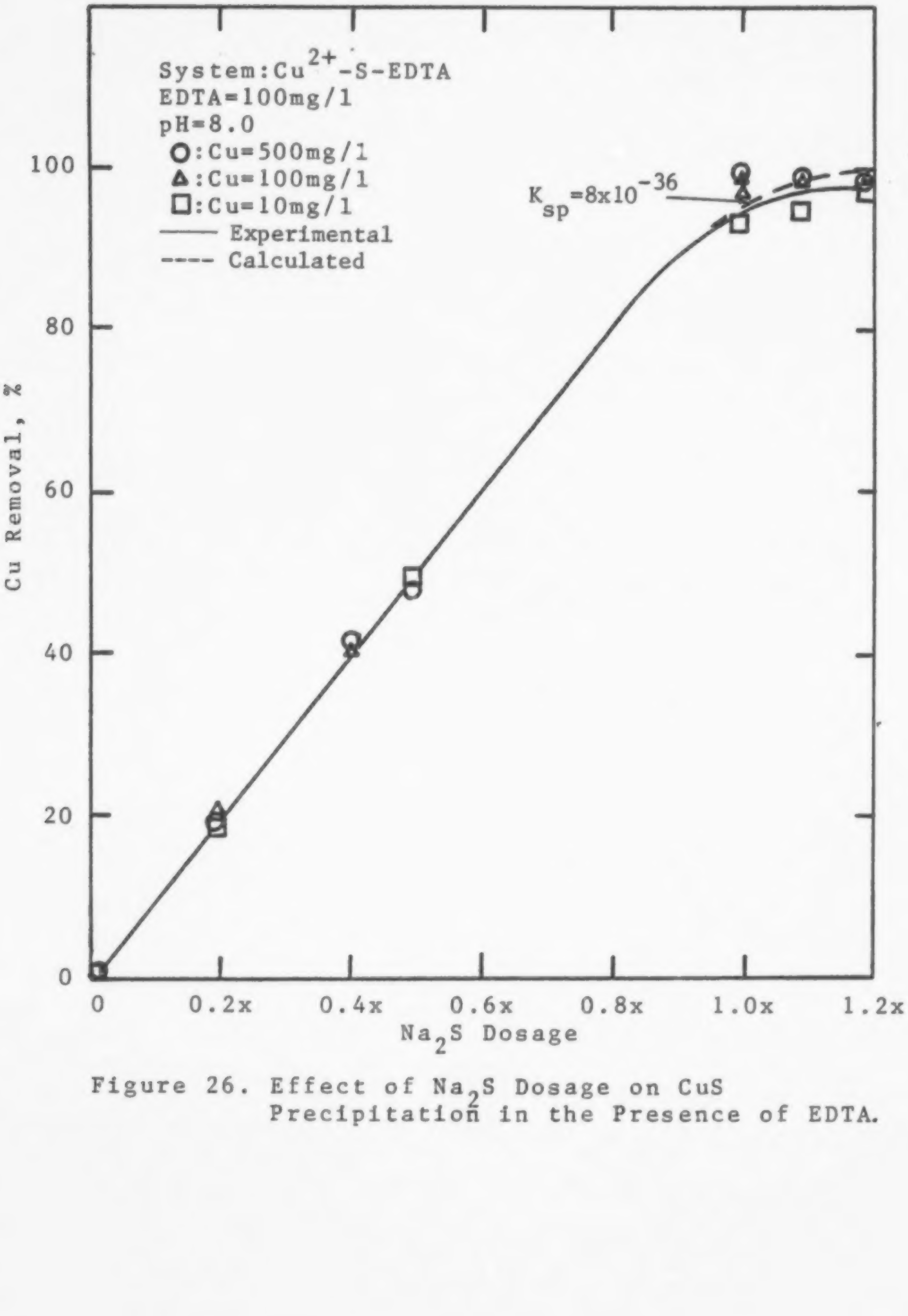

Figure 26. Effect of Na_2S Dosage on CuS Precipitation in the Presence of EDTA.

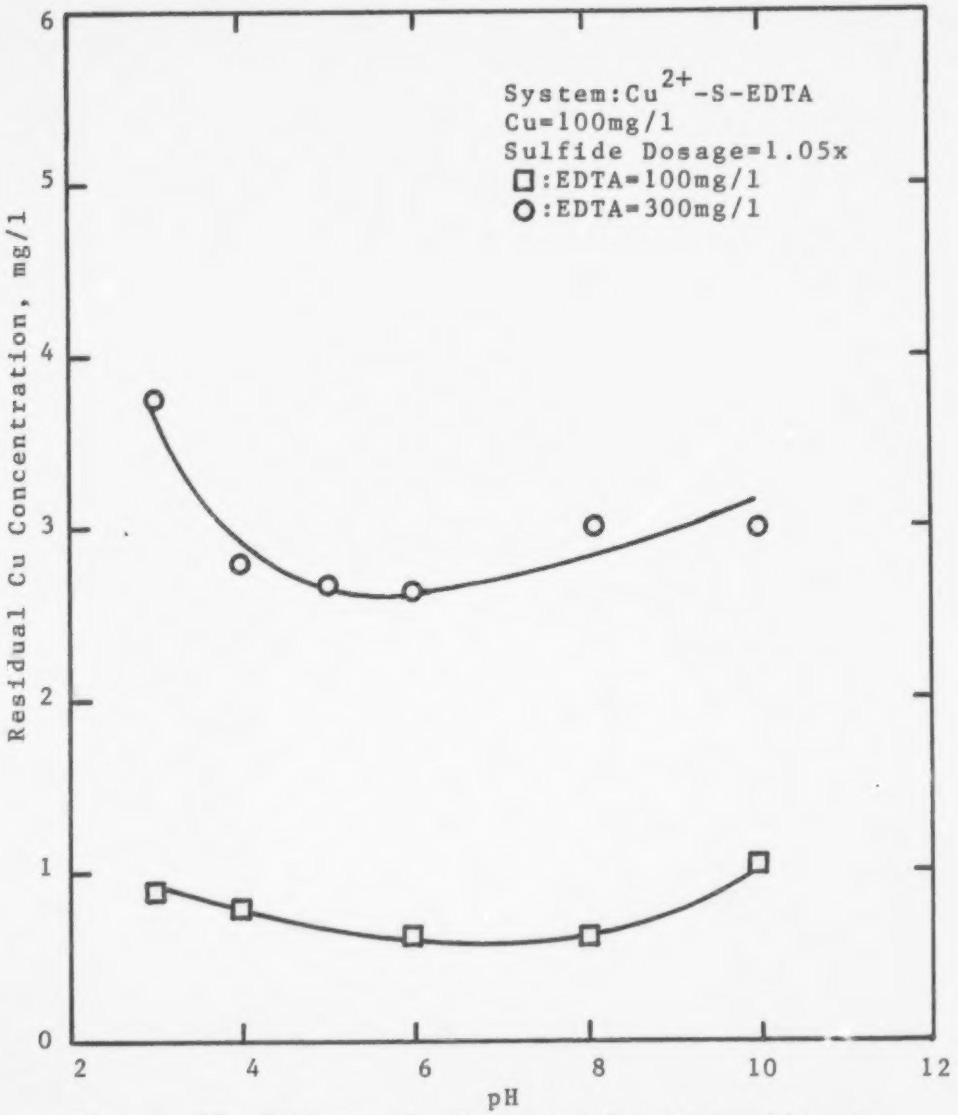

Figure 27. Effect of pH on CuS Precipitation in the Presence of EDTA.

TABLE 10. EFFECT OF pH ON CuS PRECIPITATION IN THE PRESENCE OF CITRATE

Cu Concentration = 100 mg/l

Na_2S Dosage = 1.05X

Citrate Concentration = 100 mg/l

Reaction Time = 30 minutes

pH	Residual Cu Concentration, mg/l (0.025 µm filter)
4	0.65
6	0.45
8	0.4
10	0.5

Reaction times for most Cu-chelating agent systems were short; Figure 28 shows that no change in copper concentration was observed after reaction time of 5 minutes. But in the presence of high concentrations (greater than 300mg/l) of citrate, the residual copper concentration increased dramatically when reaction time was greater than 20 minutes, see Figure 29. In order to find out whether the increase of residual copper concentration would result from the oxidation of copper sulfide at high citrate concentration, one experiment was carried out under nitrogen environment (closed system). The result in Figure 30 shows the same behavior as in an open system and thus the increase in solubility was not due to CuS oxidation.

It should be noted that copper formed very fine precipitate with sulfide, Table 11 shows the extent of difference in residual copper concentration by using various sizes of filter paper. For example, 62mg/l of copper was left by using 0.45 μm filter, only 0.8mg/l of copper was left in the filtrate by using 0.025 μm filter paper. This indicates the use of very fine filter paper is necessary to separate copper sulfide particles. In order to increase the particle size of copper sulfide, the addition of some polymers or flocculation technique would be necessary.

The theoretical solubility of copper sulfide in the

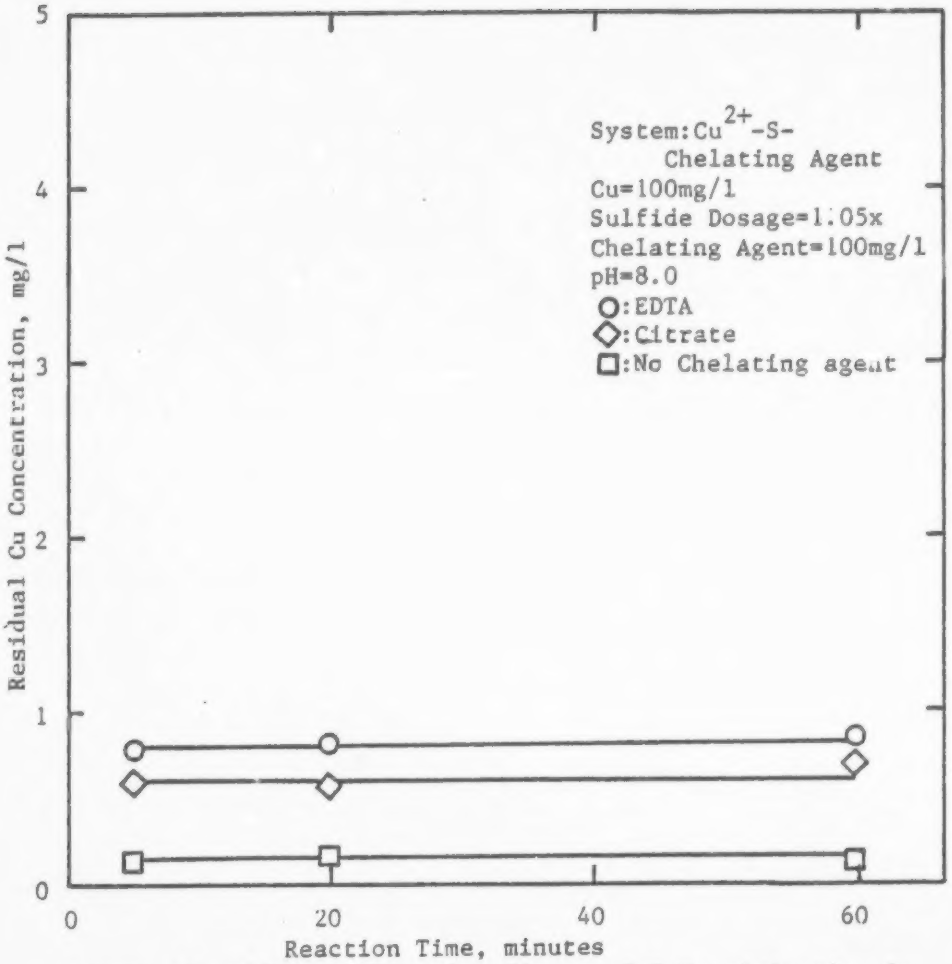

Figure 28. Effect of Reaction Time on CuS Precipitation in the Presence of Chelating Agents.

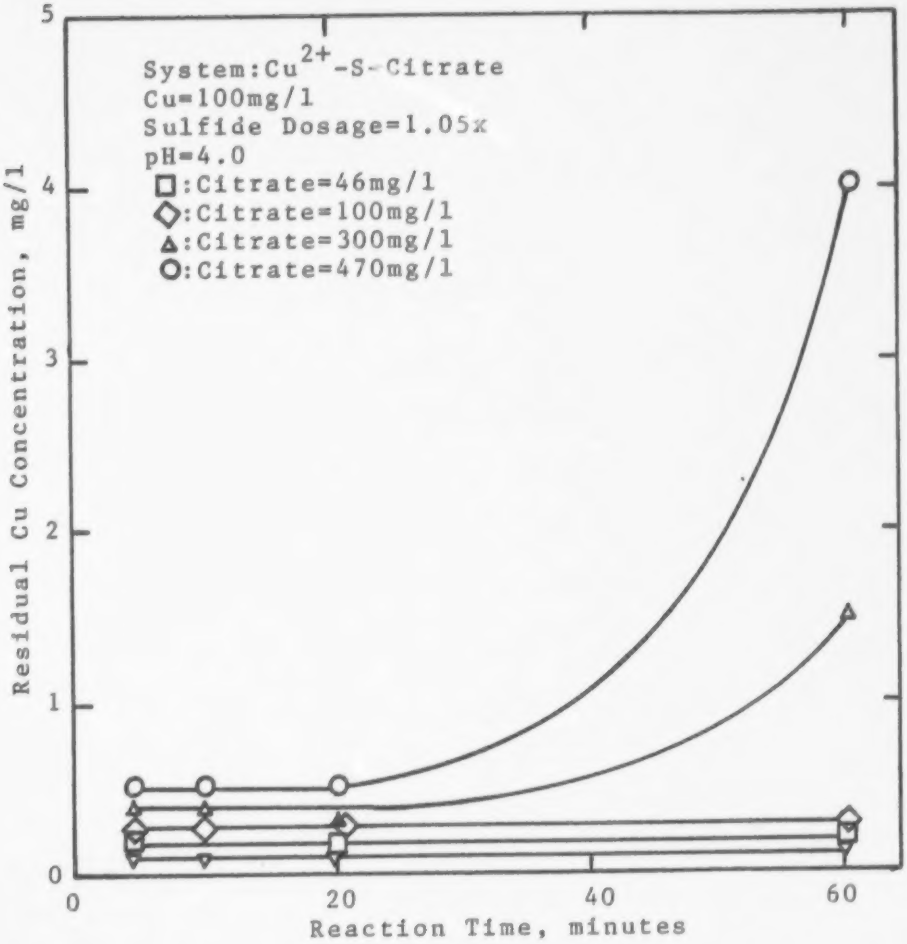

Figure 29. Effect of Reaction Time on CuS Precipitation in the Presence of Various Concentration of Citrate.

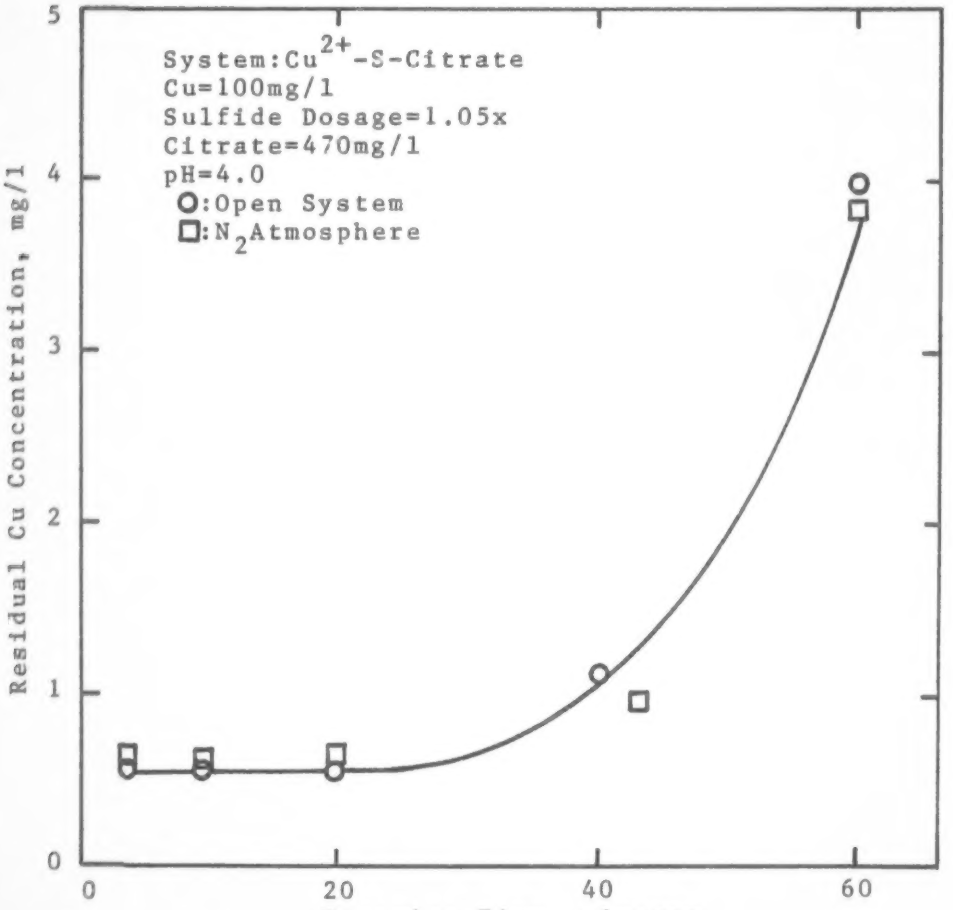

Figure 30. Comparison of CuS Precipitation in Open System and in N_2 Atmosphere for Cu-Citrate System.

TABLE 11. COMPARISON OF RESIDUAL METAL CONCENTRATIONS OBTAINED WITH THREE DIFFERENT MICROFILTERS FOR METAL-S-EDTA SYSTEM

Metal Concentration = 100 mg/l

Na_2S Dosage = 1.05X

EDTA Concentration = 100 mg/l

pH = 4.0

Reaction Time = 30 minutes

Metal Ion	Residual Metal Concentration, mg/l		
	0.025 µm	0.1 µm	0.45 µm
Zn^{2+}	13.0	13.2	13.2
Cu^{2+}	0.8	32.0	62.0
Cd^{2+}	2.1	2.2	2.2
Ni^{2+}	62.7	64.0	64.0

presence of chelating agent is less 0.001mg/l (in the presence of 100mg/l of EDTA) which is much lower than the experimental data. This can be explained that copper sulfide formed very fine particles. There were small portions of copper sulfide precipitate passed through 0.025 m filter paper and caused the higher experimental residual copper concentration.

Table 11 also shows the results for Zn, Cd and Ni ions by using various sizes of filter papers. No significant difference in residual metal concentration was observed by using either 0.025 or 0.45 μm filter paper.

Cadmium Sulfide Precipitation

Several experiments were carried out with cadmium ion. Cadmium was selected because of its high toxicity. The solubility product (K_{sp}) of CdS is about 10^{-28}, which is lower than the solubility product of ZnS. As predicted, Table 12 shows experimental results of residual cadmium concentration are much lower than zinc concentrations in the presence of 100mg/l EDTA under same experimental conditions. Experimental data for copper ion are also listed in Table 12 for comparison purposes.

TABLE 12. COMPARISON OF SULFIDE PRECIPITATION FOR VARIOUS METALS CONTAINING EDTA

Metal Concentration = 100 mg/1

Na_2S Dosage = 1.05X

Reaction Time = 30 minutes

pH =8.0

Metal I[illegible]	EDTA Concentration (mg/1)	Residual Metal Concentration (mg/1)
Zn^{2+}	100	12.8
Zn^{2+}	500	68.0
Cu^{2+}	100	0.7
Cu^{2+}	500	5.2
Cd^{2+}	100	2.1
Cd^{2+}	500	5.8
Ni^{2+}	100	20.0
Ni^{2+}	400	87.0

Table 13 shows the residual cadmium concentration after sulfide precipitation in the presence of various chelating agents. EDTA formed most stable chelates with cadmium ion among four chelating agents used in the study. Experiments were also conducted at pH 4 for cadmium in the presence of various concentration of EDTA. Results are shown in Figure 31. At EDTA concentration greater than 100mg/l, about 4% (molar ratio) of EDTA formed chelates with cadmium. For example, if a solution contains 200mg/l of EDTA (about 0.6 mM) and 100mg/l of Cd (about 0.9 mM), a sulfide dosage of 1.0-1.05x will result in Cd residual concentration of (4% x 0.6 mM) x 112mg/m mole = 2.7mg/l.

Figure 32 shows the pH effect on residual cadmium concentration by sulfide precipitation for solution containing 100mg/l of EDTA. Satisfactory removals of cadmium were obtained over a broad pH range.

Nickel Sulfide Precipitation

Nickel was chosen because of the high solubility of nickel sulfide ($K_{sp} = 2.0 \times 10^{-21}$). Several experiments were carried out for Ni-S-EDTA system. The pH effect on NiS precipitation is shown in Figure 33 in the presence of 100mg/l of EDTA. At pH 4, residual nickel concentration was about 35mg/l,

TABLE 13. EFFECT OF CHELATING AGENTS ON CdS PRECIPITATION

Cd Concentration = 100 mg/l

Na_2S Dosage = 1.05X

Chelating Agent Concentration = 100 mg/l

Reaction Time = 30 minutes

Chelating Agent	Residual Metal Concentration (mg/l) (0.45 μm filter)	
	pH = 4.0	pH = 8.0
EDTA	1.4	2.1
Citrate	0.5	0.9
Gluconic Acid	0.45	0.65
Tartrate	0.25	0.35
No	0.1	0.3

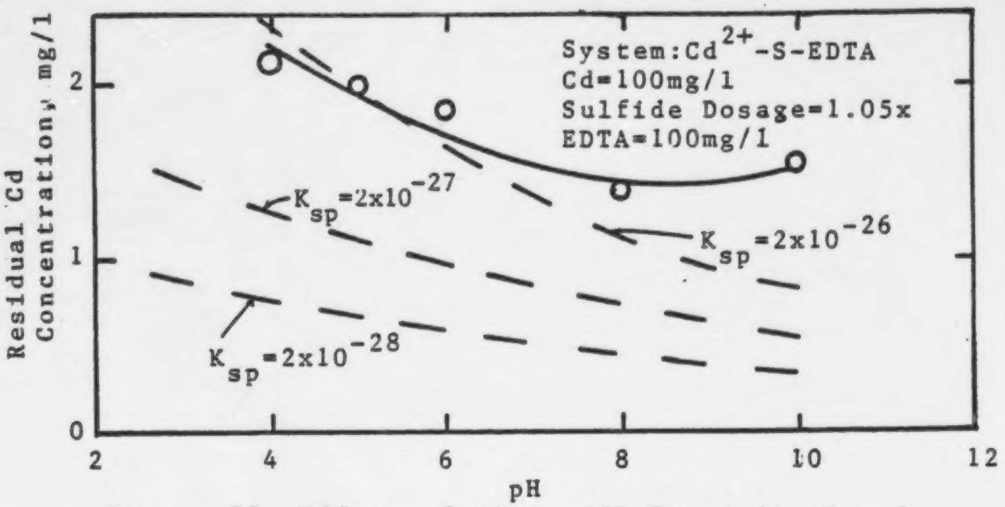

Figure 32. Effect of pH on CdS Precipitation in the Presence of EDTA.

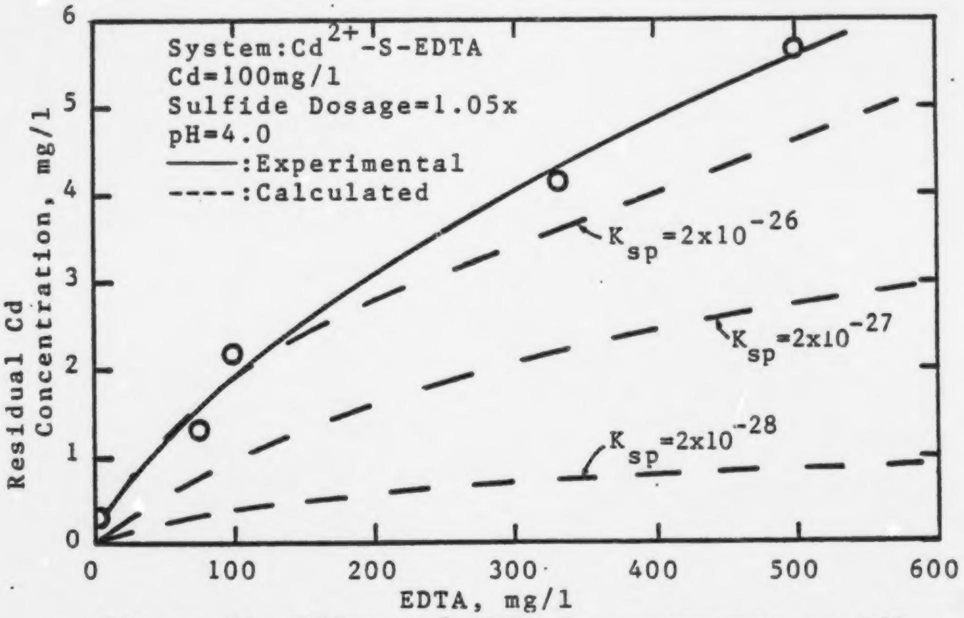

Figure 31. Effect of EDTA Concentration on CdS Precipitation.

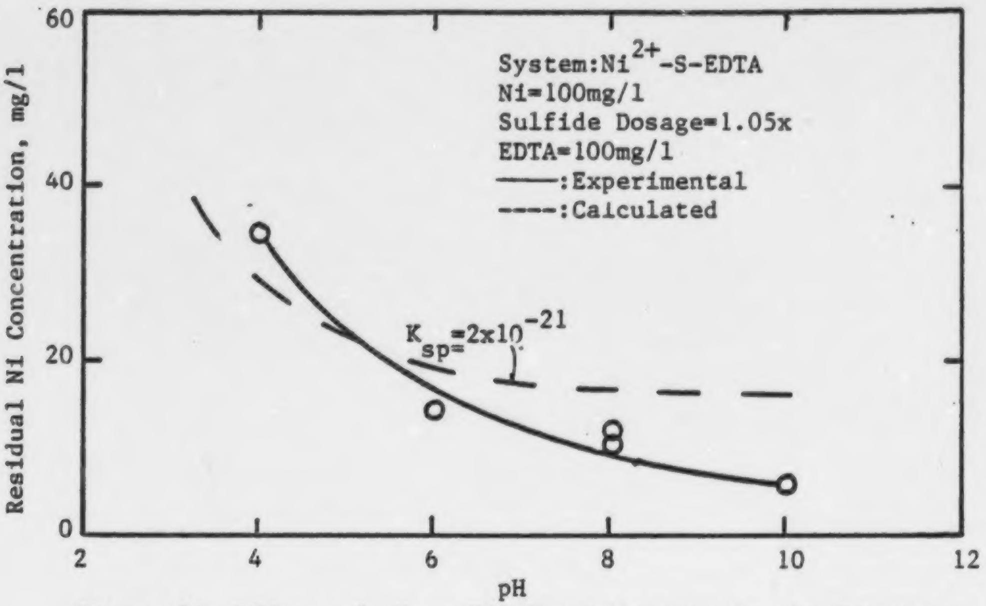

Figure 33. Effect of pH on NiS Precipitation in the Presence of EDTA.

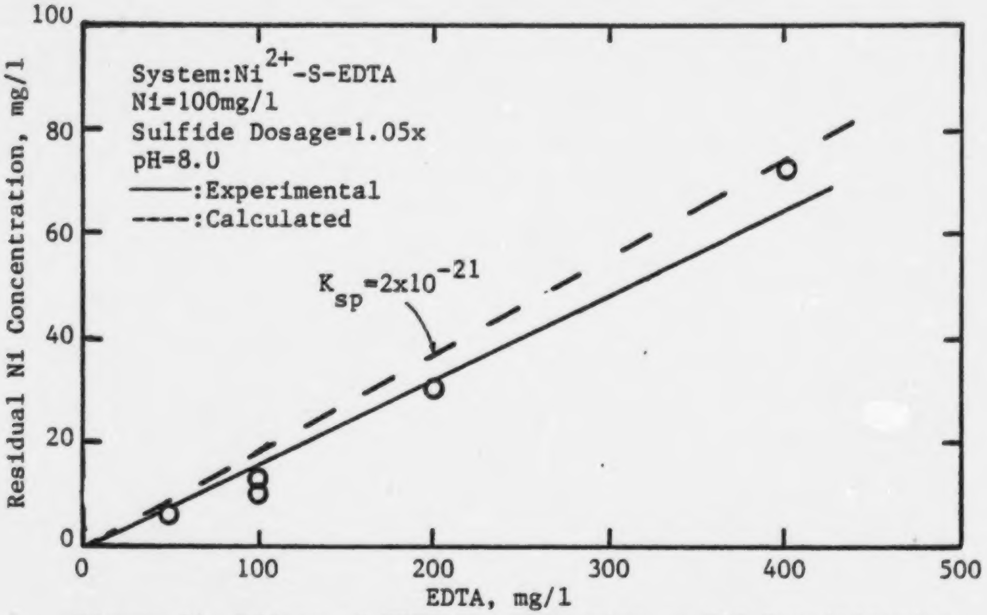

Figure 34. Effect of EDTA Concentration on NiS Precipitation.

considerably higher than copper and cadmium. At pH greater than 6, residual nickel concentration was about 10mg/l even at pH 10. Figure 34 shows high concentration of EDTA in solution resulted in very poor precipitation of nickel. If the amount of EDTA present is 500mg/l, no precipitation would occur for solution containing 100mg/l of Ni. From Figure 34, it can be concluded that if the molar ratio of EDTA/Ni greater than 1.0, almost no sulfide precipitation would occur. The dotted line shown in Figure 33 and 34 indicate the calculated solubilities based on literature K_{sp}. In contrast to Zn and Cd, experimental Ni results fit in well with these calculated values based on literature K_{sp}.

Nickel sulfide precipitation was found to be a strong function of reaction time. This effect is shown in Figure 35 for various Ni-S-chelating agent systems. After a reaction time of 5 minutes, residual nickel concentration increased with time. This phenomenon has been reported by Bhattacharyya, et al.(23) in the absence of chelating agents and can be explained that nickel sulfide obtained by precipitation is a thermodynamically unstable form (22). In the presence of oxygen, the precipitate is partially oxidized to give the disulfide NiS_2, products containing hydroxide, sulfate, etc., which are more soluble than nickel sulfide. Experiment conducted in N_2 atmosphere showed that residual Ni concentration (after NiS precipitation) did not increase with time.(Figure 35 dotted line).

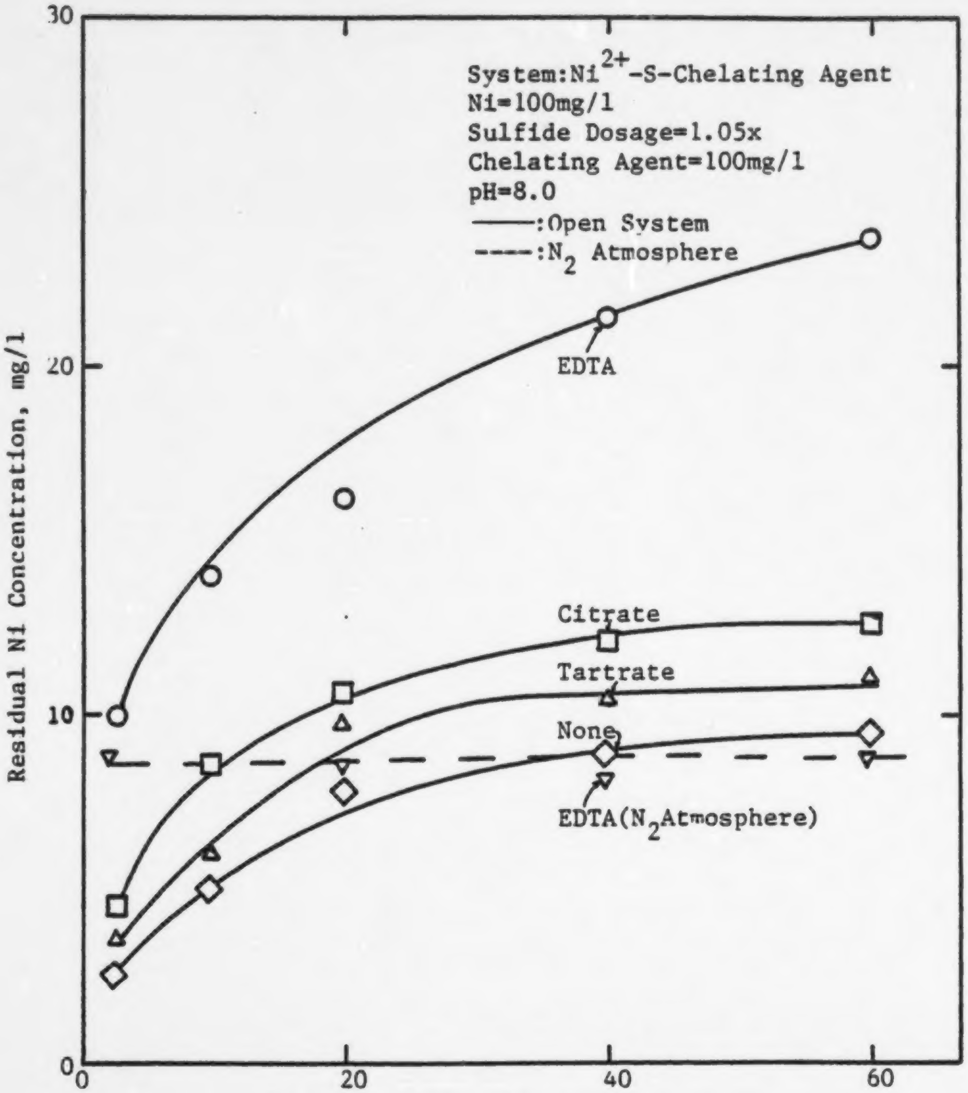

Figure 35. Effect of Reaction Time on NiS Precipitation in the Presence of Chelating Agents.

Sulfide Precipitation of Solutions Containing Multi-Metal Ions

Additional studies of metal sulfide precipitations containing more than one metal ion were carried out with and without EDTA to determine if intereactions between different metal ions caused any interference on metal sulfide precipitation.

Cu-Zn System:

Experiments with solutions containing Cu^{2+} and Zn^{2+} ions were conducted at pH 8.0 and in the presence of 200mg/l EDTA. Two different sulfide dosage were used to determine their effect on residual metal concentrations. These results are shown in Table 14. Comparing with residual metal concentrations for single metal systems when 1.05x sulfide dosage (for Cu^{2+} and Zn^{2+}) was used, the results show almost same amount of residuals were left for both systems. This indicates that the Cu and Zn mixture behaves like a single metal solution. Since Cu has higher selectivity than Zn, the use of a sulfide dosage less than 1.0x results in preferential precipitation of copper. The complete precipitation of copper sulfide at 0.8x sulfide dosage (for Cu^{2+} and Zn^{2+}) agrees well with the expected result. This indicates that CuS formation is predominant when sulfide is added into feed solution. After Cu

TABLE 14. SULFIDE PRECIPITATION OF Cu-Zn MIXTURE IN THE PRESENCE OF EDTA

pH = 8.0
Reaction Time = 30 minutes

Initial Metal Concentation, mg/l		EDTA Concentration, mg/l	Na_2S Dosage	Residual Metal Concentration, mg/l (0.1 µm filter)	
Cu	Zn			Cu	Zn
100	100	0	1.05X	0.4	0.3
100	100	100	1.05X	0.3	15.0
100	100	200	1.05X	0.4	27.0
100	100	200	0.8X	0.5	74.0
0	100	100	1.05X	---	12.0
100	0	100	1.05X	0.5-1.0	----

sulfide precipitate was nearly complete, Zn-S reaction became important. This also shows that if only 0.5x Na_2S dosage is added to the Cu-Zn mixture, only copper will precipitate as sulfide. It is interesting to note that even in the presence of EDTA, metal mixture (such as Cu-Zn) can be precipitated to recover only one metal (such as Cu from Cu-Zn mixture).

It should be noted that the mixture suspension was filtered by 0.10 μm (instead of 0.025 μm) filter paper. Complete removals of copper sulfide precipitate were obtained for all these Cu-Zn systems. This indicates the particle size of copper sulfide precipitate was aggregated (comparing with results for single metal experiments shown in Table 11) in the presence of ZnS precipitate.

Several experiments with Cu-Cd, Ni-Zn, Cd-Zn, Cu-Ni and Cd-Ni mixture were carried out with and without EDTA. Most results show no significant variation comparing with single metal systems which indicates the intereactions between these metal ions did not cause severe interference on metal sulfide precipitation; the only exception is the Cd-Ni solution which will be discussed separately.

Cd-Ni System:

A series of experiments were carried out for Cd-Ni mixture at various sulfide dosages and pH 8.0. Because Cd ion is more **selective** than Ni ion, the uses of sulfide dosage less than 1.0x should result in preferential precipitation for cadmium. But experimental results (Figure 36 and 37) show that for sulfide dosage less than 1.0x, nickel residuals were 12-14mg/l even for a dosage of 0.34x (stoichiometric dosage for Cd ion only). This can be explained that nickel ion may precipitate as hydroxide at pH 8.0. In contrast to Figure 35, it should be noted that NiS does not oxidize with time.

The residual cadmium concentrations for these experiments are shown in Figure 37. Residual concentrations are considerably higher for Cd-Ni mixture than for single metal cadmium solution (less than 0.5mg/l) under the same experimental conditions. The increase of cadmium residual may be due to the formation of Cd(HS)(OH) which is more soluble than CdS. It is possible that Cd(HS)(OH) formation is catalyzed by the presence of NiS or $Ni(OH)_2$. In order to investigate the unusual effect (observed in Figure 37) of nickel ion on the precipitation of cadmium, experiments were carried out with added nickel concentration. Results are shown in Figure 38 and 39 as a function of Ni/Cd

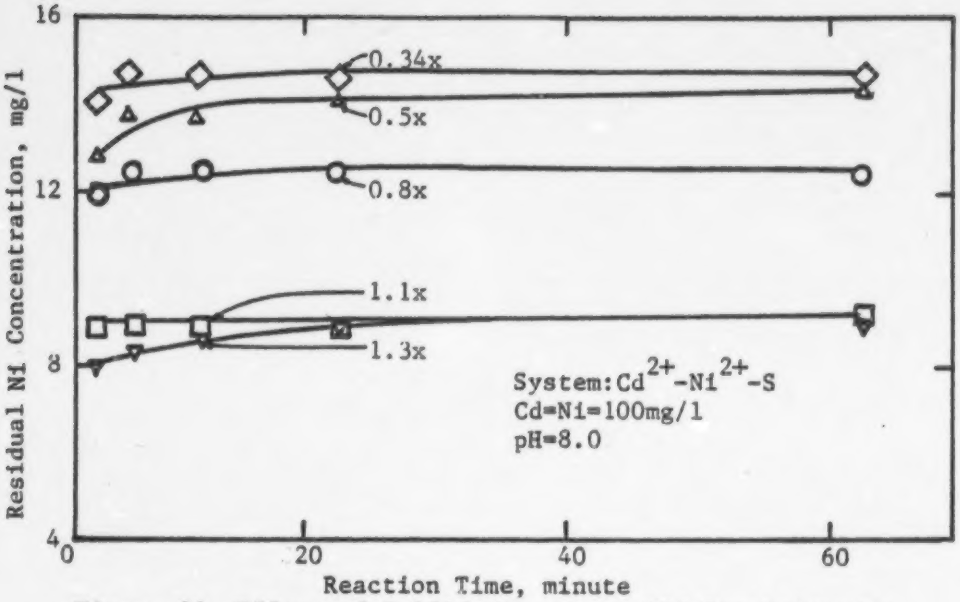

Figure 36. Effect of Sulfide Dosage on NiS Precipitation for Cd-Ni Mixture as a Function of Reaction Time.

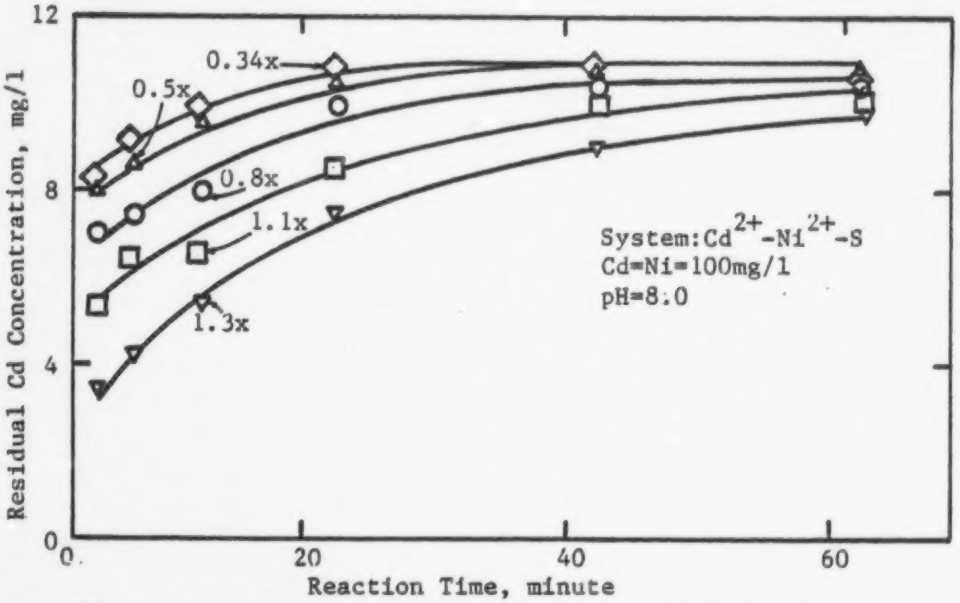

Figure 37. Effect of Sulfide Dosage on CdS Precipitation for Cd-Ni Mixture as a Function of Reaction Time.

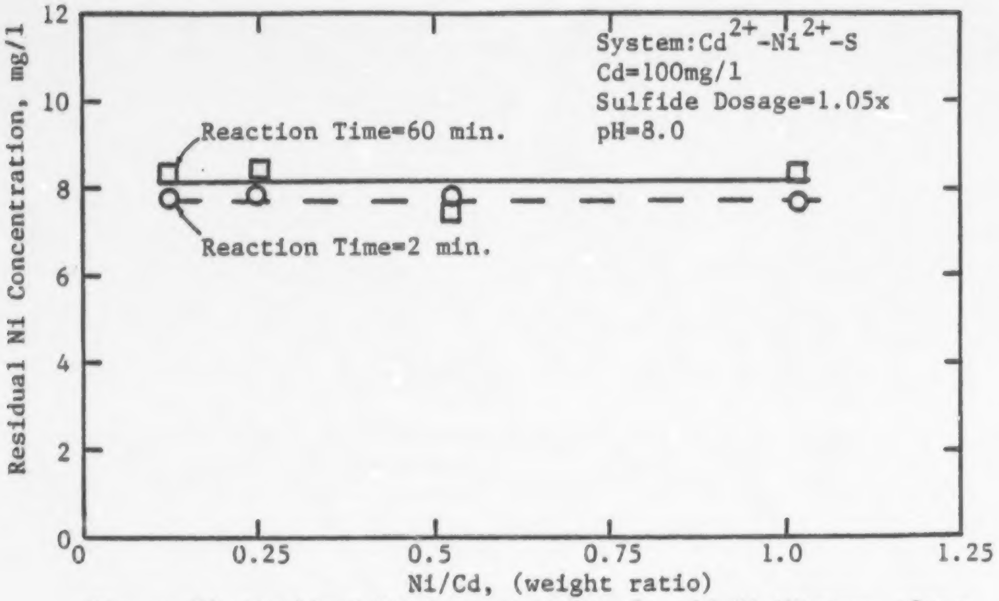

Figure 38. Residual Ni Concentration for Cd-Ni Mixture after Sulfide Treatment as a Function of Ni/Cd Ratio.

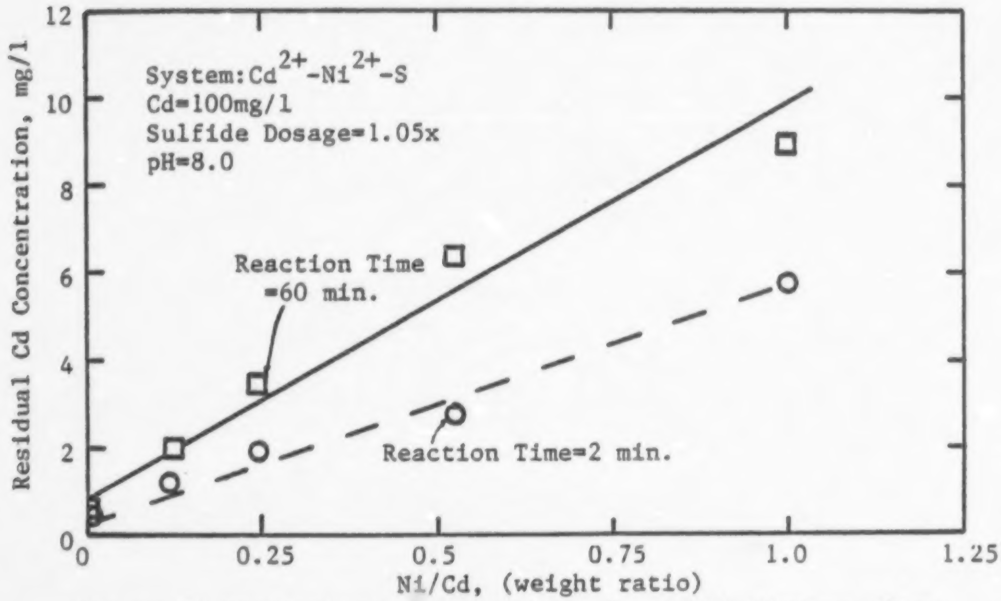

Figure 39 Residual Cd Concentration for Cd-Ni Mixture after Sulfide Treatment as a Function of Ni/Cd Ratio.

ratio. Residual cadmium concentration increases with Ni/Cd ratio.

Cu-Cd-Ni-Zn System:

Experimental results are shown in Figure 40 as a function of time after sulfide treatment of a Cu-Cd-Ni-Zn mixture. Satisfactory removals of Zn and Cu were obtained. Ni still interferes the precipitation of CdS. Figure 41 shows the experimental results with EDTA present. Copper sulfide precipitate was complete because of its high selectivity. Removal of Zn and Ni were poor (about 20mg/l residual concentration left) because of the higher solubilities of ZnS and NiS. CdS dissolution increased in the presence of Ni, which was similar to that observed with Cd-Ni system.

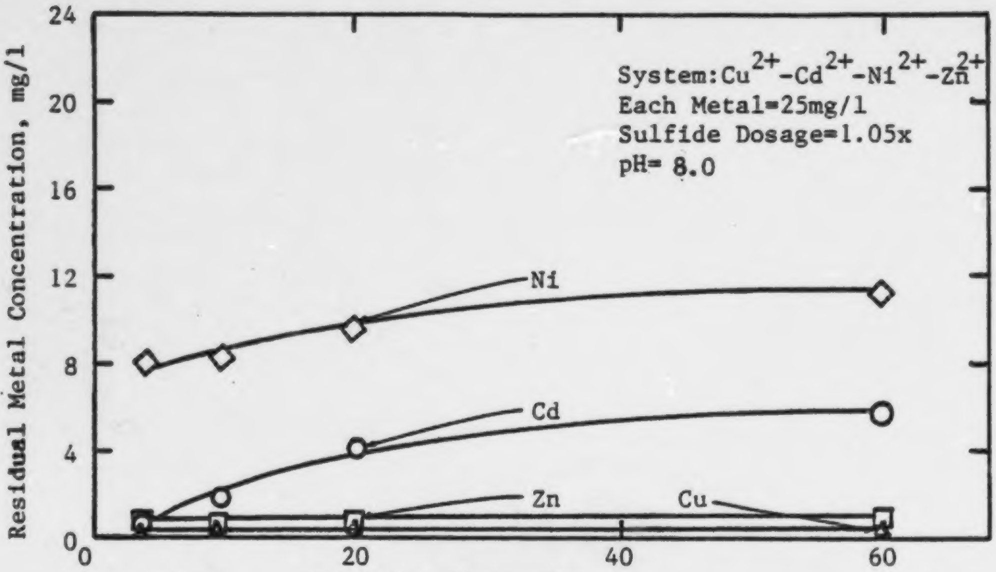

Figure 40. Effect of Reaction Time on Residual Metal Concentrations for Cu-Cd-Ni-Zn Mixture.

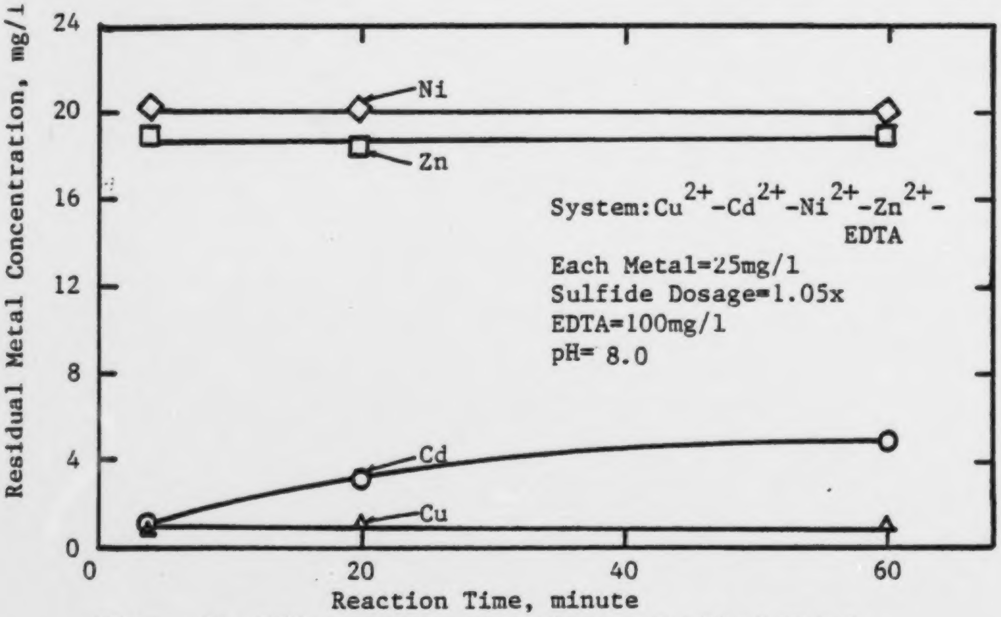

Figure 41. Effect of Reaction Time on Residual Metal Concentrations for Cu-Cd-Ni-Zn-EDTA Mixture.

Continuous Systems for Sulfide Precipitation

In order to simulate the treatment of an industrial wastewater by sulfide precipitation, several continuous experiments were conducted under various conditions. Detention time of 18 minutes (for reaction tank) and sulfide dosage of 1.05x were used in these experiments.

Single-Metal System:

Studies were carried out for Zn^{2+}, Cu^{2+}, Cd^{2+}, and Ni^{2+} ions with and without EDTA. Satisfatory removals of metal ions were obtained after sulfide treatment. Results are plotted against residual metal concentrations for batch experiments under same experimental condition (Figure 42). The residual concentrations for continuous experiments are quite similar to batch experiments (except one high Ni point). Sulfide dosage fluctuation may have caused somewhat higher residuals.

Multi-Metal System:

A mixture of Cu^{2+}, Cd^{2+}, Zn^{2+}, and Ni^{2+} ions was used in this study with and without EDTA. Results are plotted against the residual metal concentrations for batch experiments at the same operational condition shown in Figure 43. Relatively low residual metal concentrations were

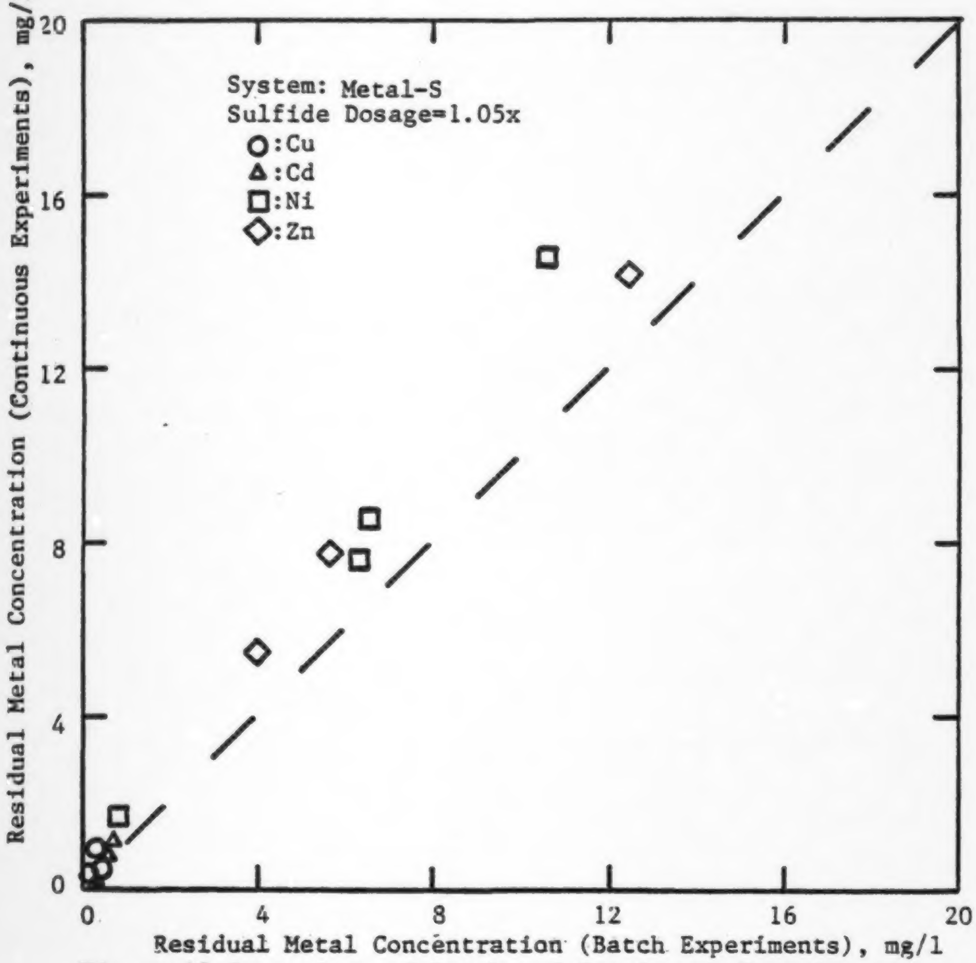

Figure 42 Comparison of Batch and Continuous Experiments under Same Experimental Conditions.

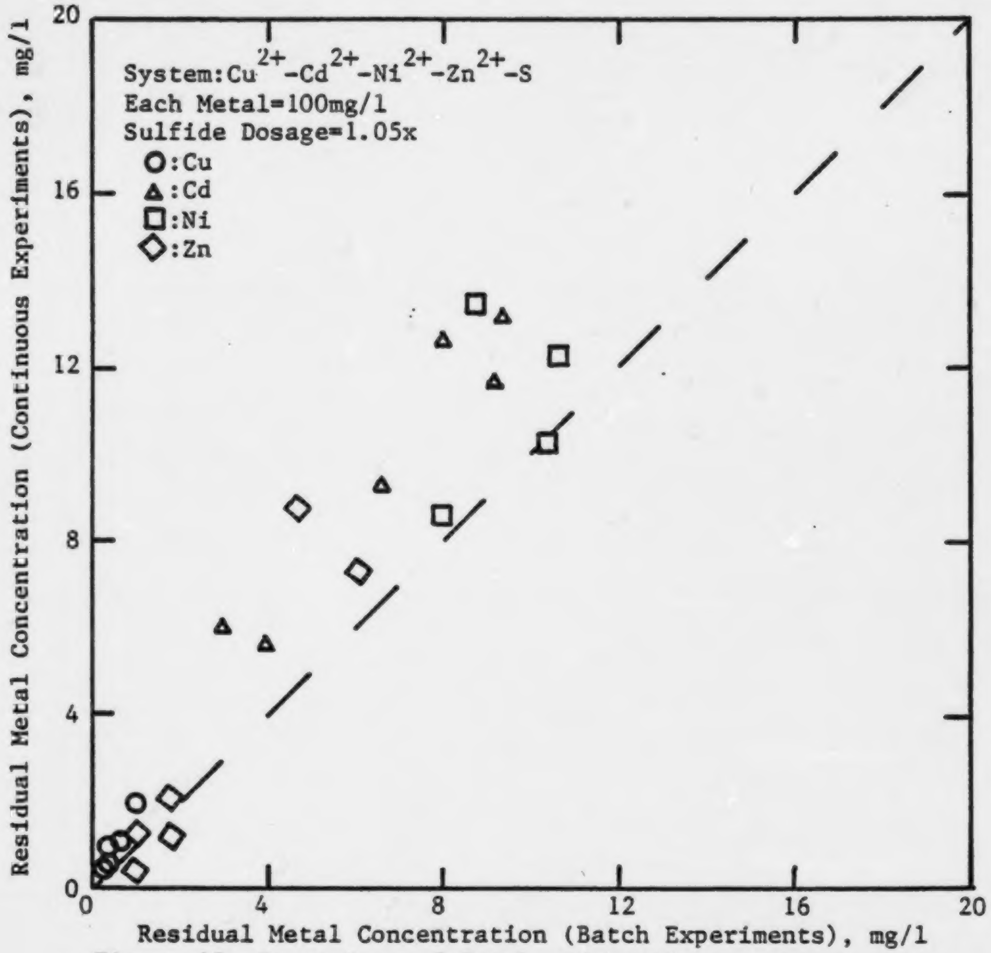

Figure 43. Comparison of Batch and Continuous Experiments for Cu-Cd-Ni-Zn Mixture under Same Experimental Conditions.

obtained for coper and zinc. But for nickel and cadmium ions, removals were not complete because of the interference between these two metal ions. Without Ni ion, low residual cadmium concentration was achieved for a mixture of Cu^{2+}, Cd^{2+}, and Zn^{2+} ions by sulfide treatment.

Another important parameter is the sedimentation of metal sulfide precipitates in the settling column. Sedimentation is one of the most used unit operations in wastewater treatment to provide primary degree of separation of solid and liquid. In this study, a 7-cm diameter, 90-cm long glass column was used as a sedimentation column. The detention time of sedimentation column at feed solution flowrate of 100 cm^3/min was 35 minutes; surface loading rate was 2.6 $cm^3/(cm^2)(min)$. The metal sulfide precipitate removals are shown in Figure 44 as a function of the initial concentration of EDTA. ZnS precipitate was removed quite effectively. The experimental data show about 20-30% of Cu, 60-80% of Cd, and 60-100% of Ni precipitate were removed by sedimentation. The presence of EDTA improved the sedimentation of copper and nickel sulfides which may be explained that EDTA aggregated the particle sizes of copper and nickel precipitates. The sedimentation characteristics for each metal sulfide are also useful for selective metal separation from solutions containing more than one metal after sulfide treatment (for example, separation of zinc

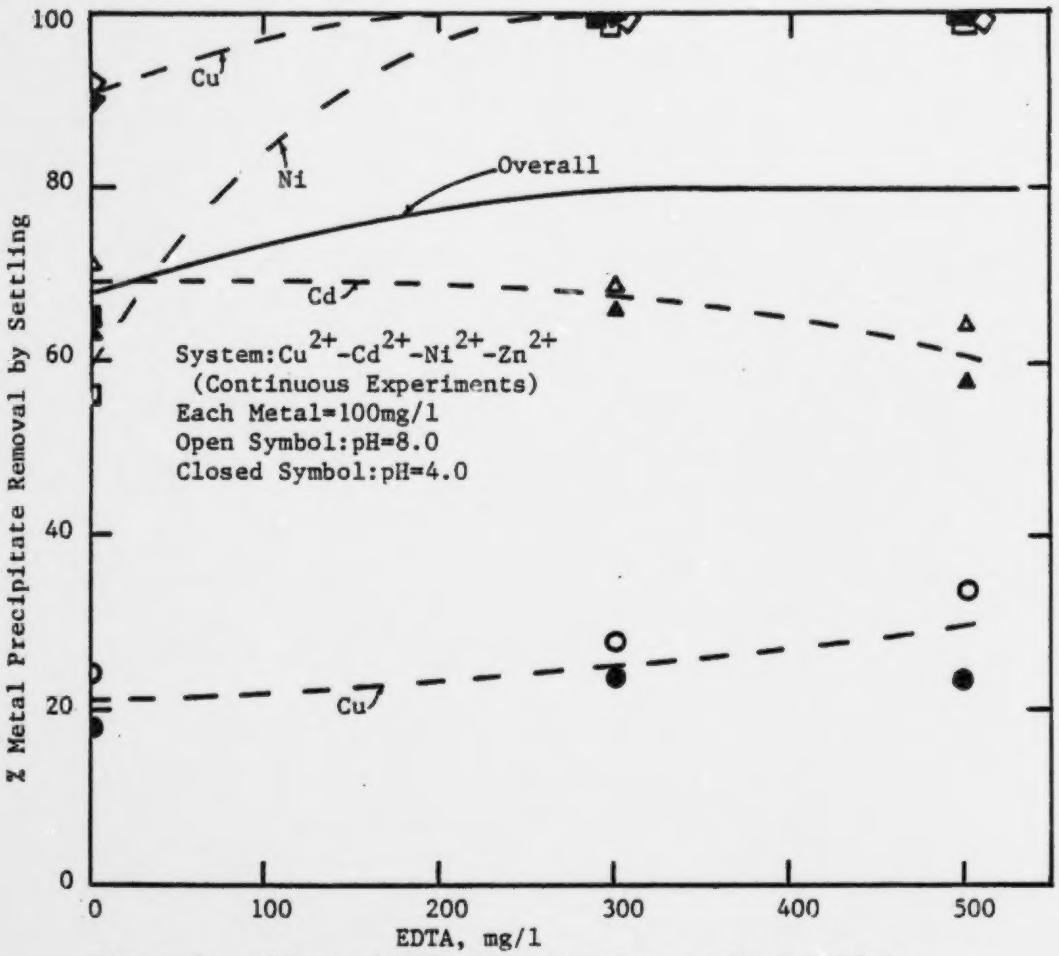

Figure 44. Effect of EDTA Concentration on Metal Sulfide Precipitate Settling Characteristics for Cu-Cd-Ni-Zn Mixture.

from copper sulfides by settling may be feasible). The overall removal of metal ions are also shown in Figure 44. Over 60% of metal sulfides were removed by sedimentation before filtration. This indicates sedimentation can be used as a preliminary step to separate metal sulfide particles before filtration or centrifugation.

Sludge rise rate (which is related to subsidence velocity) was also measured. The sludge rise rate of a mixed metal sulfide precipitate in the absence of EDTA was three times higher than that was observed with EDTA. For example, precipitation of a mixture containing Cu-Cd-Ni-Zn (100mg/l each) and 500mg/l of EDTA and subsequent settling (at 2.6cm/min overflow rate) showed a sludge rise rate of 0.4cm/min.

SECTION 6

SUMMARY AND CONCLUSIONS

An extensive investigation was conducted for metal sulfide precipitation in the presence of chelating agents to establish the relative interference effect of metal chelates. The experimental results were compared with theoretical equilibrium solubilities for various operational conditions and reaction systems. Sulfide precipitation was shown to be a feasible process to achieve a high degree of separation for most heavy metals even in the presence of strong chelating agents (such as EDTA). The formation of metal chelates was found to be strongly influenced by the types of metal ions, the types of chelating agents, the concentration of chelating agents present in the solution, and pH values.

For traditional hydroxide precipitation, the presence of chelating agents often causes severe interference on the extent of separation due to precipitation. Figure 45 shows the theoretical solubility of $Cu(OH)_2$ in the presence of chelating agents. For example, even with weak chelating agents, such as gluconic acid, considerable increase in residual concentration was observed at pH 9. Another feature of hydroxide precipitation is that satisfactory removal efficiency may not be possible unless the pH value is controlled within a narrow range. Figure 46 summarizes the effect of pH and chelating agents on residual metal concentration after sulfide precipitation for various metal ions. In the absence of chelating agents the selectivity of metal sulfide precipitation is Cd > Cu > Zn > Ni. The reversal of Cu and Cd selectivity is mainly due to the formation of fine precipitates with Cu. In the presence of chelating agents, the solubility sequence is Cu > Cd > Zn > Ni. For strong chelating agents (such as EDTA), experimental results shows that metal chelate formation becomes a strong competitive

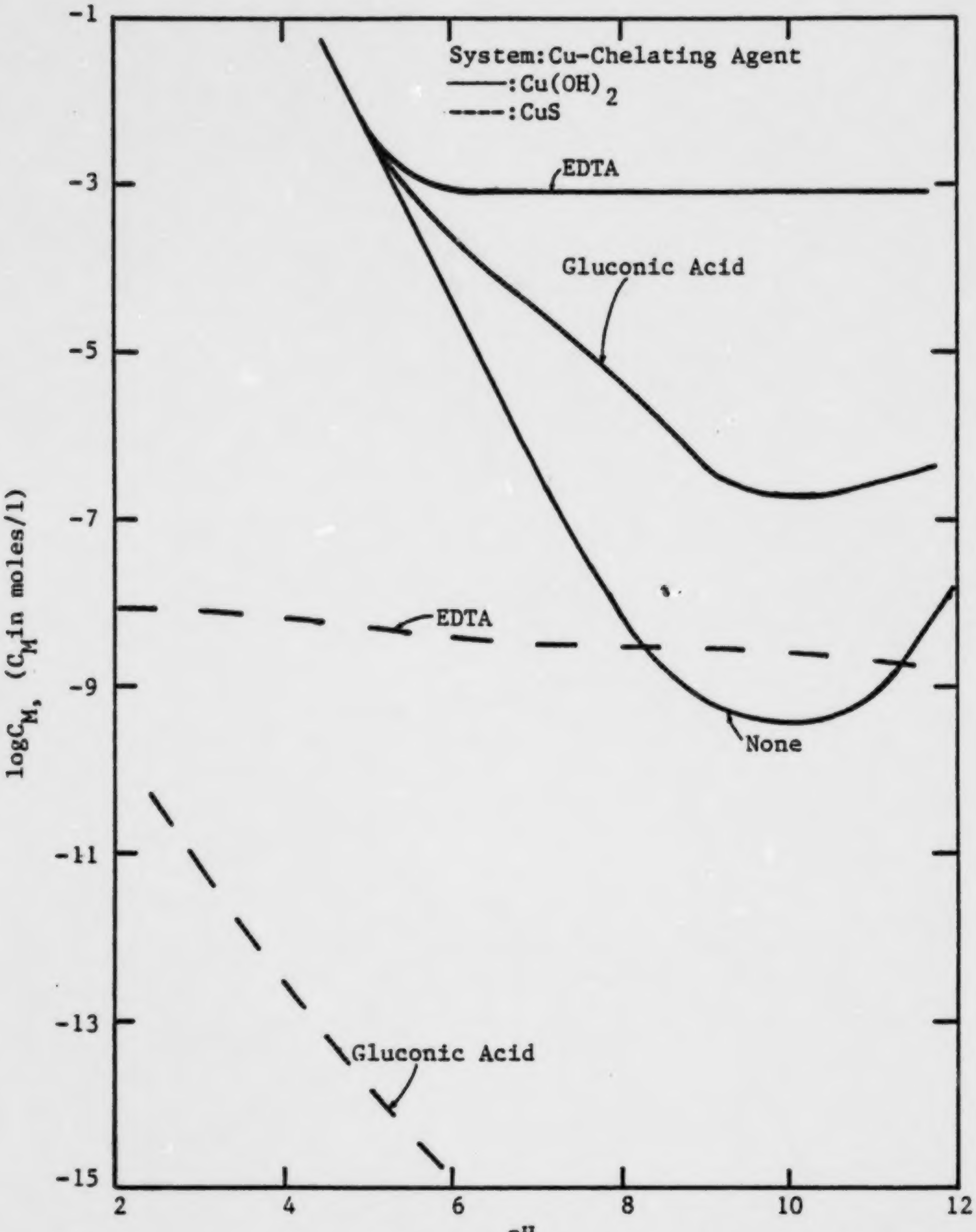

Figure 45. Calculated Solubilities of $Cu(OH)_2$ and CuS as a Function of pH in the Presence of Chelating Agent.

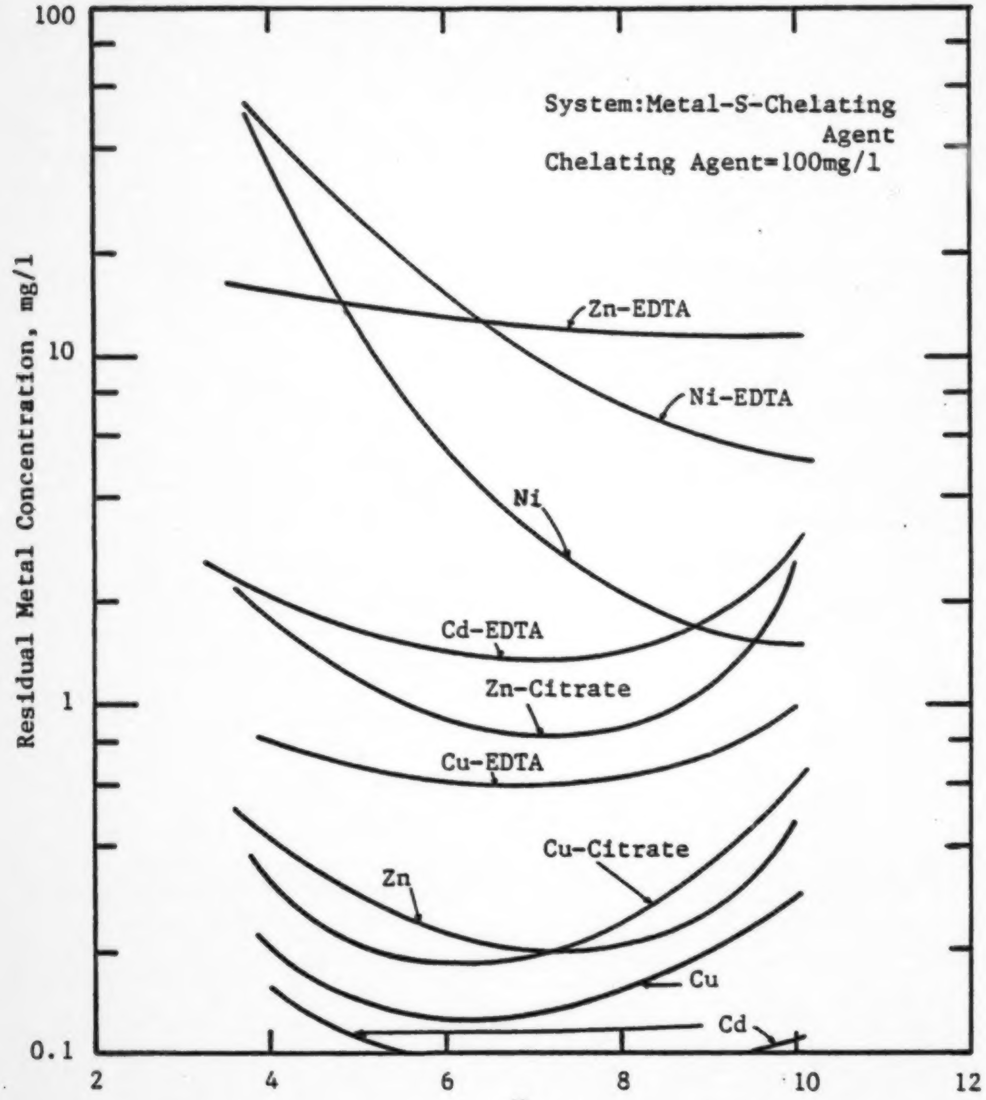

Figure 46. Effect of Chelating Agents and pH on Metal Sulfide Precipitation (Experimental).

reaction to sulfide precipitation, especially for Ni and Zn. High percentage of EDTA formed chelates with Ni and Zn ions (for Ni: 80%, Zn: 70% of EDTA formed chelates), while highly insoluble sulfides (CuS and CdS) were less influenced by the side reaction. Figure 46 also showed pH effect on sulfide precipitation was less than that observed with hydroxide precipitation. Satisfactory removal can be obtained for some metals (such as Cu and Cd) even at low pH 4.

It should be noted that NiS precipitation was a strong function of reaction time (Figure 35) in open systems (presence of oxygen). Minimum residual Ni concentration was obtained with reaction times of about 5 minutes. NiS oxidation can be prevented in closed systems (or N_2 atmosphere); the equilibrium residual Ni concentration corresponded to that obtained at 5 minutes with an open system. In the presence of high citrate concentration (300 mg/l), partial dissolution of CuS occurred above a reaction time of 20 minutes.

Comparing the experimental values of residual metal concentration with theoretical solubilities (Figures 9, 13, 14, and 15), experimental data were always higher than the theoretical values except for Ni. For copper, this deviation may be due to the formation of fine particles with its effect on K_{sp}. For Zn^{2+} and Cd^{2+}, an important aspect relating to deviation from theoretical solubility is the value of literature solubility product constants used are based on the solubility product constants for aged metal sulfide precipitates. However, in these studies, the metal sulfide precipitates formed were fresh precipitates of varying morphology. The K_{sp} of fresh precipitates may be 1 to 3 log cycle higher than those for aged precipitates. Figures 47 and 48 show the comparison of ZnS experimental data to calculated values for aged precipitate $K_{sp} = 1.6 \times 10^{-24}$ and corrected $K_{sp} = 1.6 \times 10^{-22}$ respectively. With Cd, higher K_{sp} values again provided the best fit with the experimental data (Figure 49) while Ni fitted in well with those predicted by literature K_{sp} (Figure 50). For some elements (such as Zn), different structures of precipitates display different K_{sp}. This may also cause the variation of residual concentration with those predicted by theoretical calculations.

Since the formation of metal chelates occurs as a side reaction to sulfide precipitation, all reactions concerning a metal-chelating agent system can be included and expressed by a conditional stability constant which is assumed as constant only under given pH (Figure 2). The experimental residual concentrations are plotted against $(K')(K_{sp})$ for many metal-chelating agent systems and shown in Figure 51. Very low $(K')(K_{sp})$ values (for example, most Cu systems) indicate weak chelation compared to sulfide precipitation. Figure 51 shows the low $(K')(K_{sp})$ values (for example, most Cu systems) indicative of chelation compared to sulfide precipitation. On the other hand, higher $(K')(K_{sp})$ values (for example, Ni-EDTA system) indicate strong chelation compared to sulfide precipitation. Figure 51 shows the decreasing trend in residual metal concentration with decrease in $(K')(K_{sp})$ values and the correlation obtained with the corrected and literature K_{sp} values.

The multi-metal mixture studies showed most mixture behaviors were the same as individual salts except for Cd-Ni system where nickel interfered the precipitation of Cd. A comparative diagram for Cd residuals obtained with four different systems is shown in Figure 52. Residual Cd concentration was a strong function of reaction time for Ni containing systems. From the multi-mixture studies, it appears that

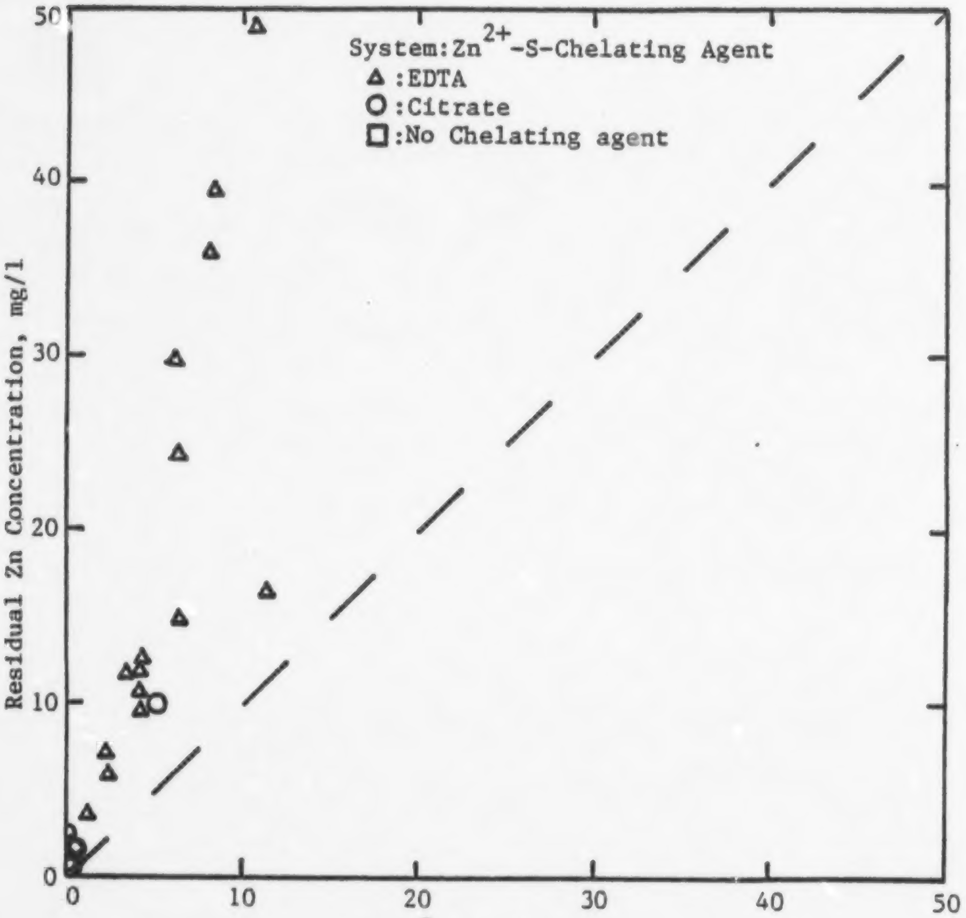

Figure 47. Comparison of Calculated and Experimental Results for ZnS Precipitation ($K_{sp}=1.6\times10^{-24}$).

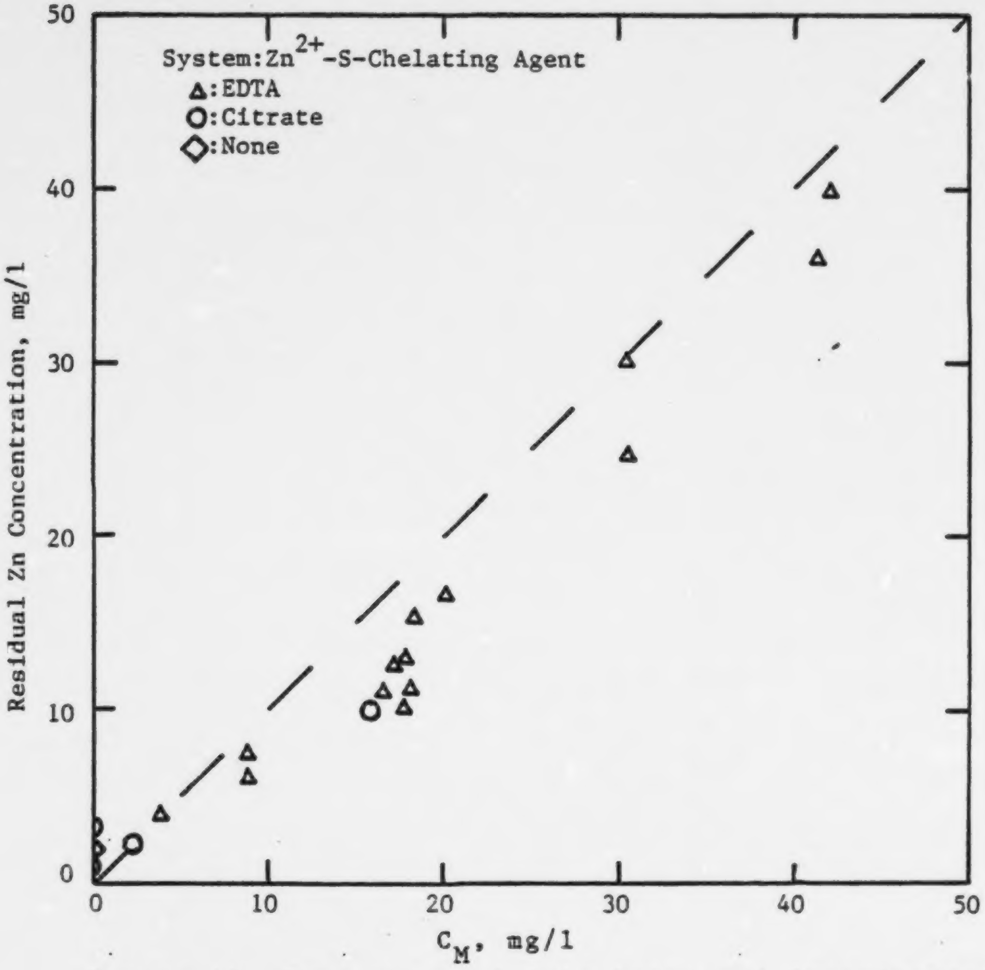

Figure 48. Comparison of Calculated and Experimental Reault for ZnS Precipitation ($K_{sp}=1.6\times10^{-22}$).

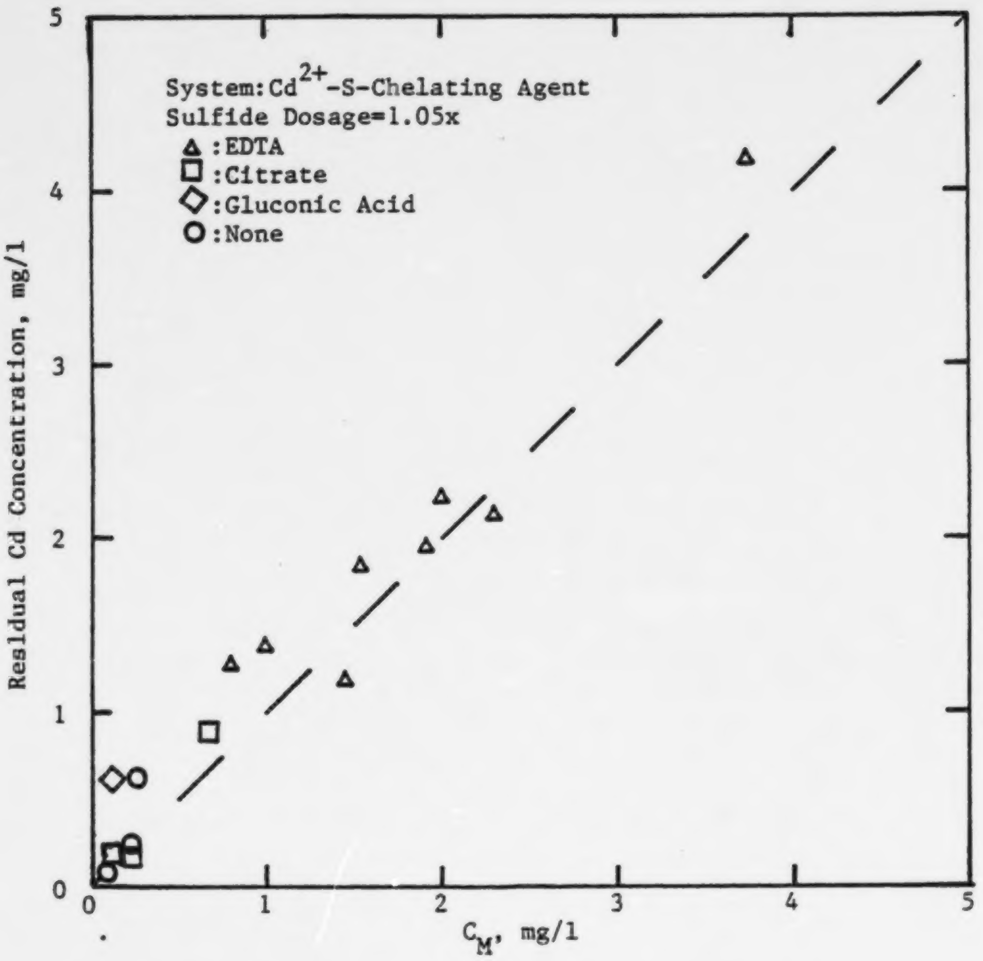

Figure 49. Comparison of Calculated and Experimental Results for CdS Precipitation ($k_{sp}=2\times10^{-26}$).

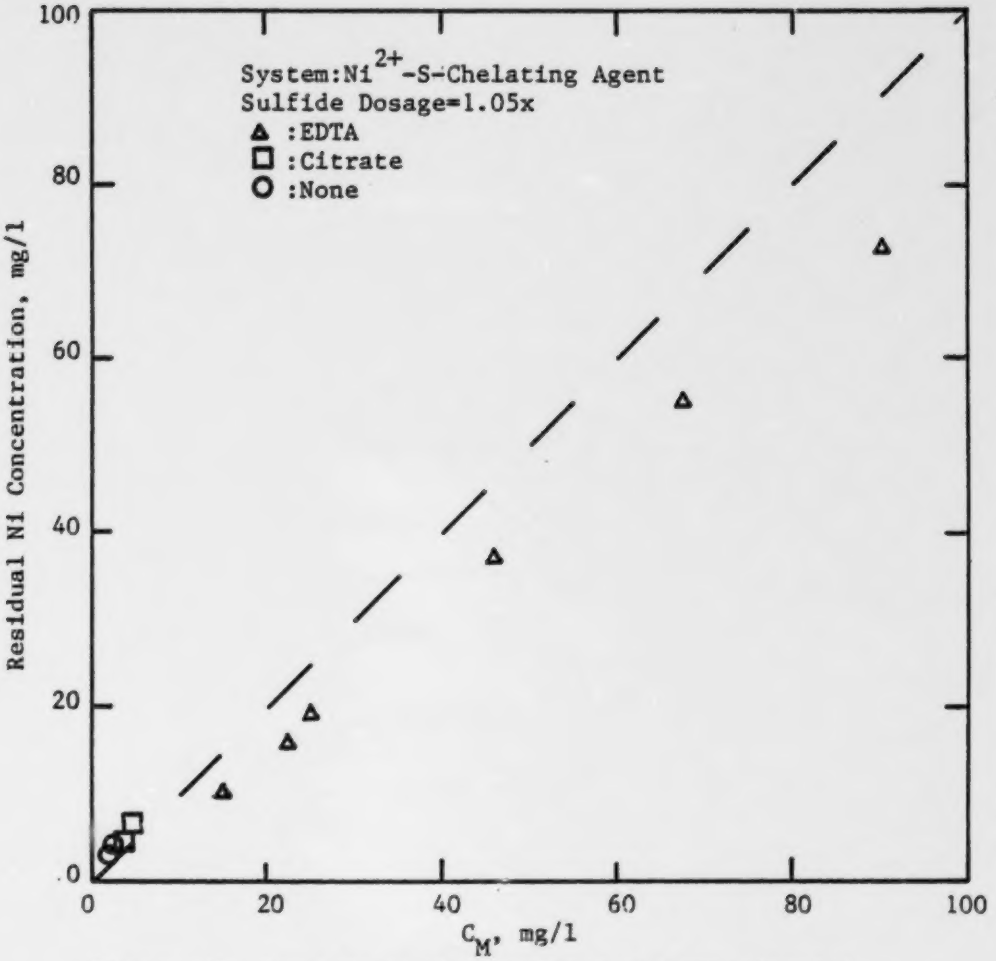

Figure 50. Comparison of Calculated and Experimental Results for NiS Precipitation using Literature K_{sp}.

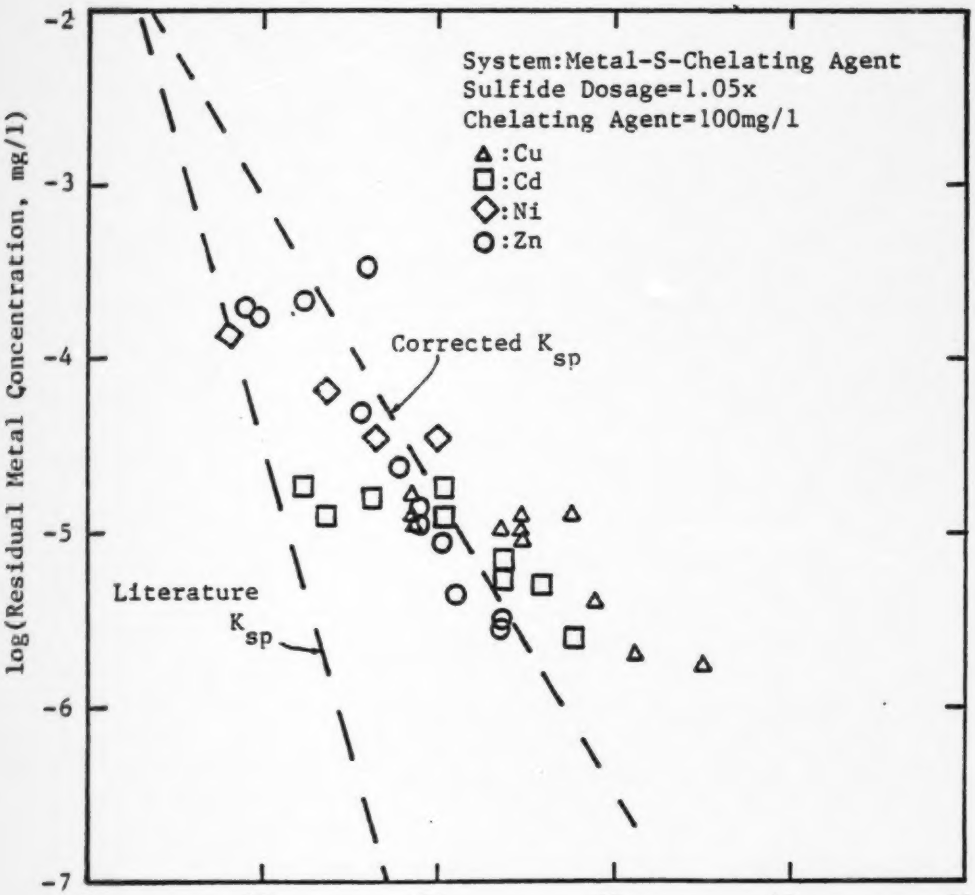

Figure 51. Relationship between Residual Metal Concentrations and Conditional Stability Constant x K_{sp}.

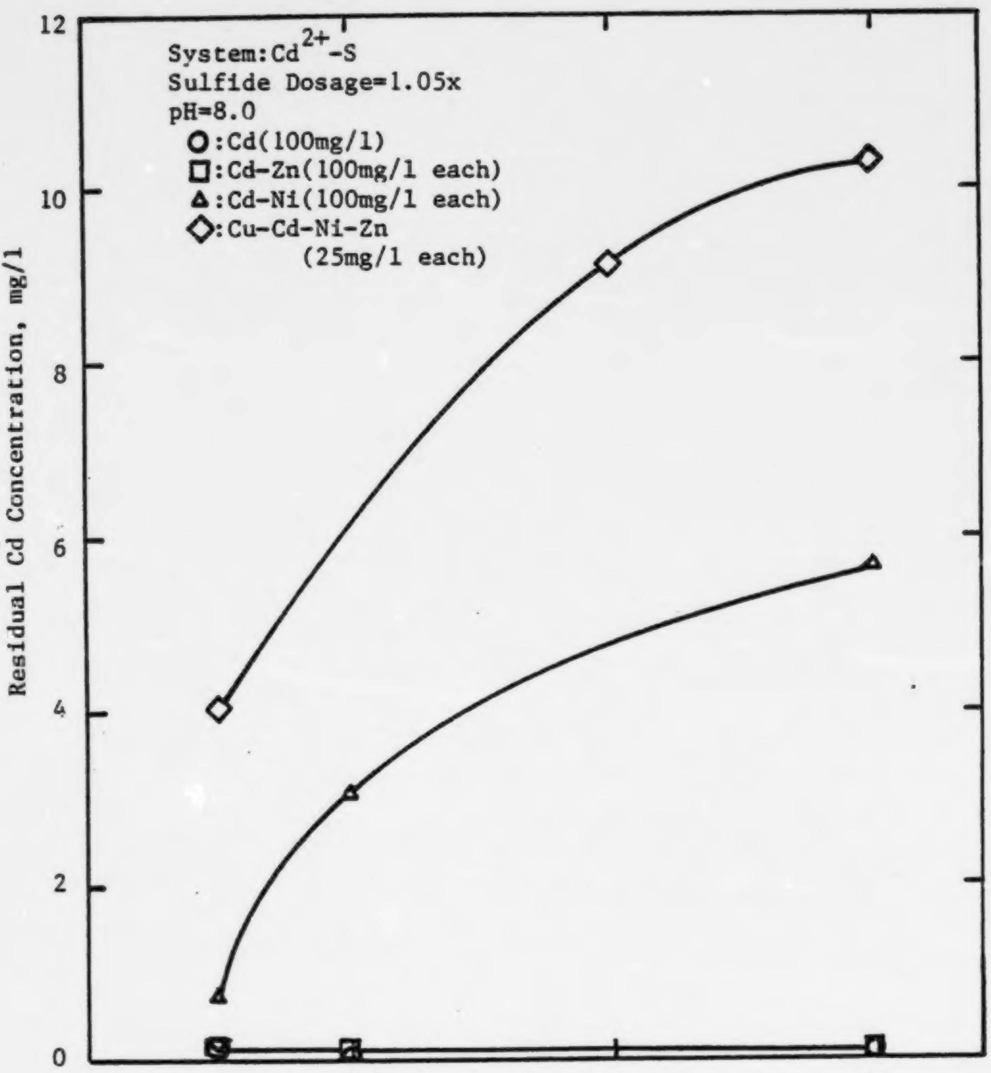

Figure 52. Effect of Zn, Ni,and Cu on CdS Precipitation.

selective metal separation from a mixture may be feasible by the addition of chelating agents. The selectivities of metal sulfide precipitation in the mixture are: CuS > CdS > ZnS > NiS. By proper adjustments of pH value, chelating agent concentration and Na_2S dosage, selective separations could be obtained.

The sulfide precipitation studies in the continuous unit showed that settling is an adequate process to provide primary degree separation of solid and liquid before filtration. The removal efficiency of ZnS precipitate was 90%, whereas CuS removal was only 20-30%. Presence of chelating agent also enhanced sludge settling characteristics.

The important conclusions are summarized as follows:

- Sulfide precipitation offered satisfactory removal for various heavy metals in the presence of chelating agents over a broad pH range (pH 4 - 10).
- Nickel sulfide precipitation was a strong function of reaction time; best removal was obtained at a reaction time of about 5 minutes.
- In the presence of nickel ion, cadmium sulfide precipitation was not complete if reaction time was allowed to exceed 2 minutes.
- Because of the different selectivities of metal ions with sulfide, separation of metals is believed to be feasible even in the presence of chelating agents.
- Settling process to separate particles after sulfide precipitation is effective for all sulfides except CuS.
- Use of extensive computer calculations (equilibrium residual metal concentration) showed that freshly precipitated CuS,

CdS and ZnS (except NiS) have higher solubilities than that predicted by literature solubility product values based on aged precipitates.

REFERENCES

1. Dean, J.D., Bosqui, F.L., and Lanouette, K.H., "Removal Heavy Metals from Waste Water", Environ. Sci. Tech., 6, 518 (1972).

2. Patterson, K.E., "Traditional vs. State-of-the-Art Methods of Treating Wastewaters Containing Heavy Metals", AICHE Symp. Series, 73, No. 166, 384 (1977).

3. Rouse, J.V., "Removal of Heavy Metals from Industrial Effluents", ASCE. Env. Div., 102, 929 (1976).

4. Patterson, J.W., "Wastewater Treatment Techonology", Ann Arbor Science Publisher, Ann Arbor, Michigan 1975.

5. Bhattacharyya, D., Jumawan, A.B., and Grieves, R.B., "Separation of Toxic Heavy Metals by Sulfide Precipitation", Sep. Sci. and Tech., 14, 441 (1979).

6. Bhattacharyya, D., Sund-Hagelberg, C., Schwitzebel, K., and Craig, F.B., "Removal of Heavy Metals, Arsenic and Fluoride from Smelter Effluents by Sulfide-Lime Precipitation", Proceeding Industrial Wastes Symposia, Water Pollution Control Federation (1980).

7. Bhattacharyya, D., Jumawan, A., Sun, G., and Schwitzebel, K., "Precipitation of Sulfide: Bench-Scale and Full-Scale Experimental Results", AICHE Symo. Series, 77(No.209), 31 (1981).

8. Lantz, J.B., :Evaluation of a Developmental Heavy Metal Waste Treatment System", Naval Construction Battalion Center Report R-314-40-6, (1979).

9. Robinson, A.K., and Sum, J.C., "Sulfide Precipitation of Heavy Meatls", EPA report, Grant No. S805413 (1979).

10. Schlauch, R.M., and Epstein, A.C., "Treatment of Metal Finishing Wastes by Sulfide Precipitation", EPA 600/2-79/049 (1977).

11. "Summary Report Control and Treatment Technology-Sulfide Precipi-Tation", EPA 625/8-80/003 (1980).

12. Robinson, A.K., "Sulfide vs. Hydroxide Precipitation of Heavy Metals from Industrial Wastewater", First Annual Conference Adv. Pollu. Cont. U.S. EPA(Cincinnati), 59(1978).

13. Bhattacharyya, D., and Jumawan, A., "Sulfide Precipitation to Treat Non-Ferrous Metal Production Wastes", EPA Interim Reports, Grant No. R 804568 (1979).

14. Anderson, J. R., and Weiss, C. O., "Method for Precipitation of Heavy Metal Sulfides", U.S. Patent 3,740,331 (1976)

15. Sun, G., "Precipitation of Heavy Metal and Arsenic with Sodium Sulfide: Effect of Sulfite-Sulfide Interaction on Metal Separation", Thesis, Lexington, Kentucky (1980).

16. Inczedy, J., "Analytical Applications of Complex Equilibria", Wiley & Sons Inc., New York (1976).

17. Ringbom, A., "Complexation in Analitical Chemistry", Wiley & Sons Inc., New York (1963).

18. Cheng, G., "Ultrafiltration of Heavy Metal Complexes with Negatively-Charged Noncellulosic Membranes", Thesis, Lexington, Kentucky (1980).

19. Lange's Handbook of Chemistry, 11th, ED., J.A. Dean (Ed.), McGraw-Hill Book Co., New York (1973).

20. Baes, C. F. Jr., and Mesmer, R. E., "The Hydrolysis of Cations", Wiley-Interscience Publisher, New York (1976).

21 "Stability Constant of Metal-Ion Complexes", (Special Publication No. 17), Chemical Society, London (1964).

22. Nickless, G., "Inorganic Sulfur Chemistry", Elsevier Publ., New York (1968).

23. Bhattacharyya, D., Sun, G., Shin, J. H., "Application of Sulfide Precipitation for the Removal of Heavy Metal from Industrial Wastewaters", Proc. 2nd World Congress of Chemical Engineering, 6, 548 (1981).